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(54) **SYSTEMS AND METHODS FOR COMBINATORIAL SYNTHESIS AND SCREENING OF MULTIELEMENT MATERIALS**

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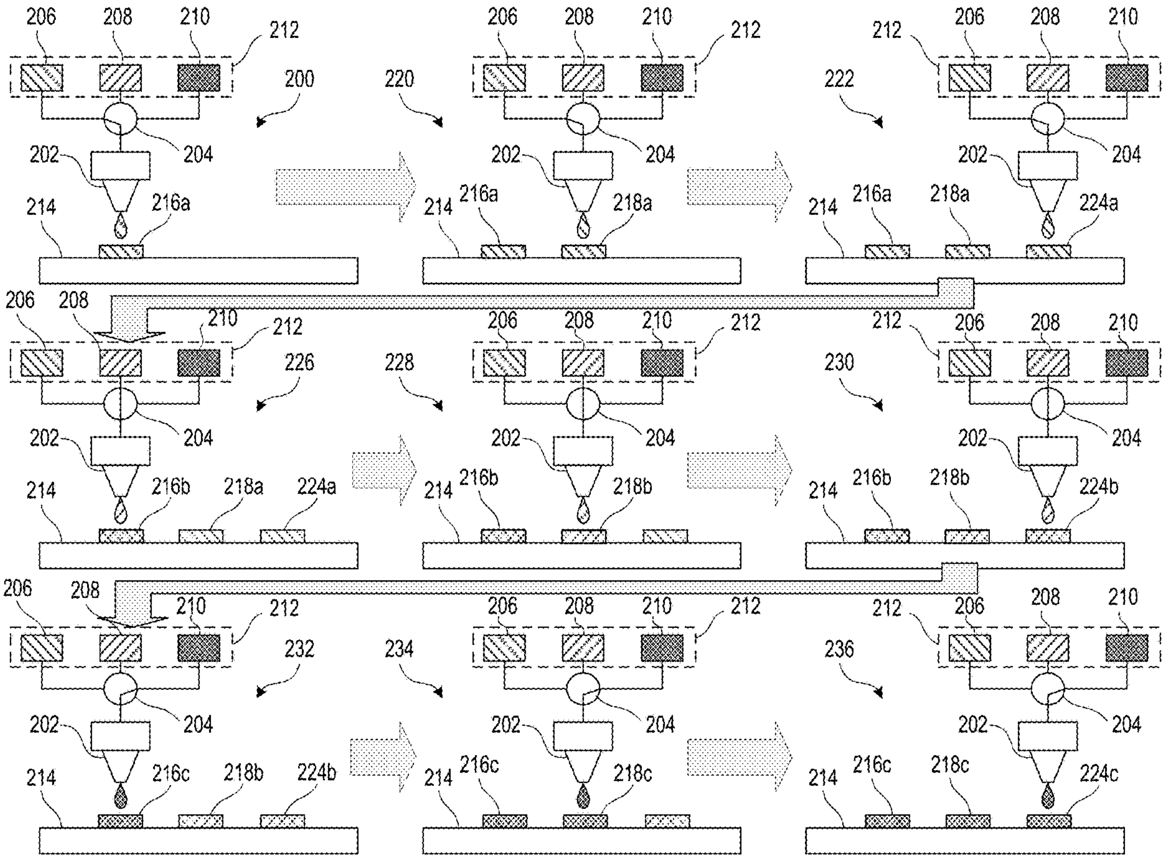
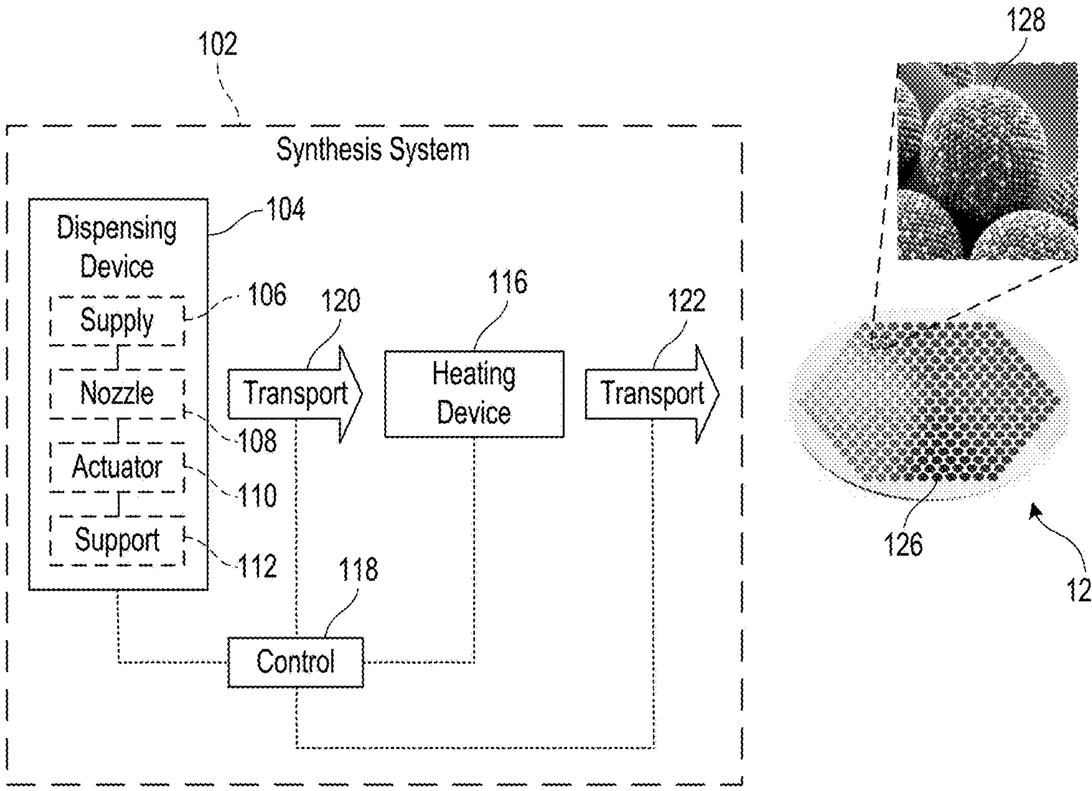
(57) **ABSTRACT**

Precursors for forming a plurality of multielement materials of different compositions can be deposited on different portions of a common substrate according to a combinatorial approach. The substrate can be subjected to a thermal shock, thereby converting the deposited precursors into separate multielement materials on the substrate. The thermal shock can be a temperature greater than or equal to 500° C. and a duration less than 60 seconds. In some embodiments, each multielement material can be tested with respect to an electrical property, a chemical property, or an optical property. Based on the results of the testing, a composition of a multielement material can be determined for use in a predetermined application, such as use as a catalyst, a plasmonic nanoparticle, an energy storage device, an optoelectronic device, a solid-state electrolyte, or an ion conductive membrane.

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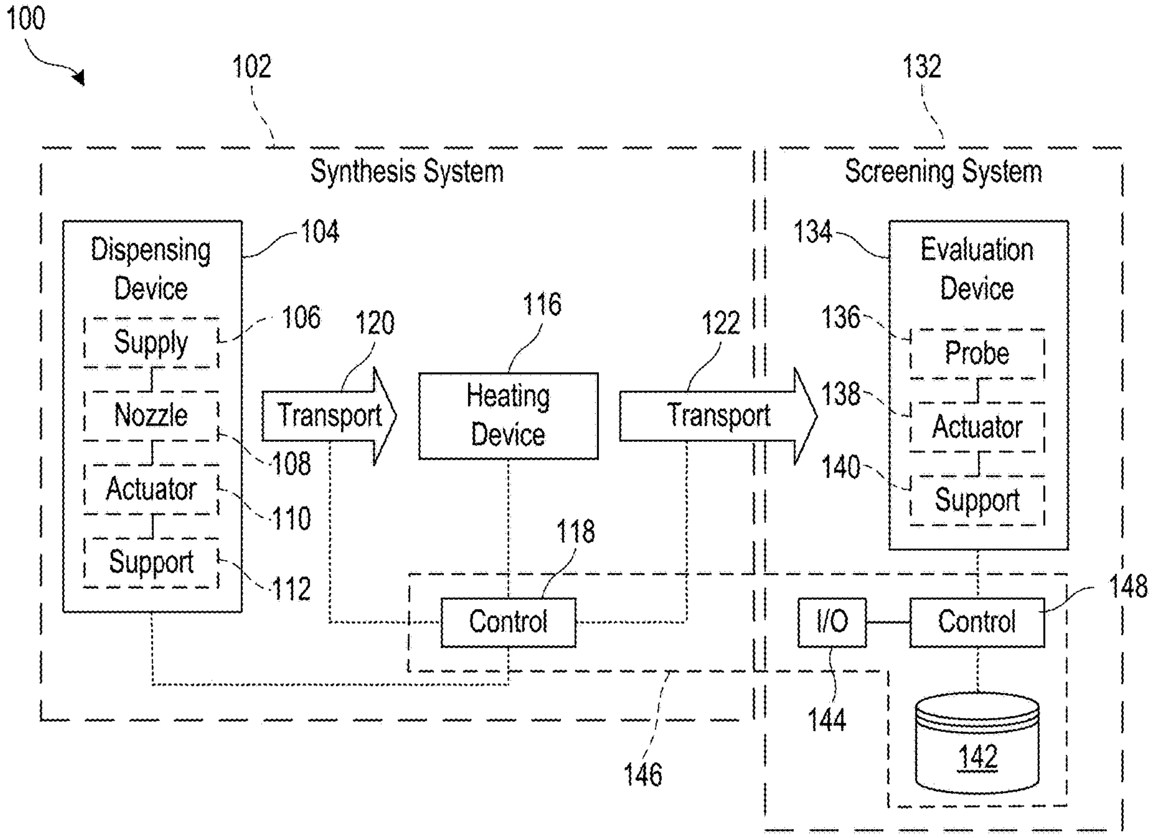
Synthesis System
Dispensing Device
104
106
Supply
Nozzle
108
Actuator
110
Support
112
120
Transport
116
Heating Device
122
Transport
118
Control
128
126
124

FIG. 1A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Screening System
Dispensing Device
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Nozzle
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Actuator
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Support
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Transport
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Heating Device
122
Transport
134
Evaluation Device
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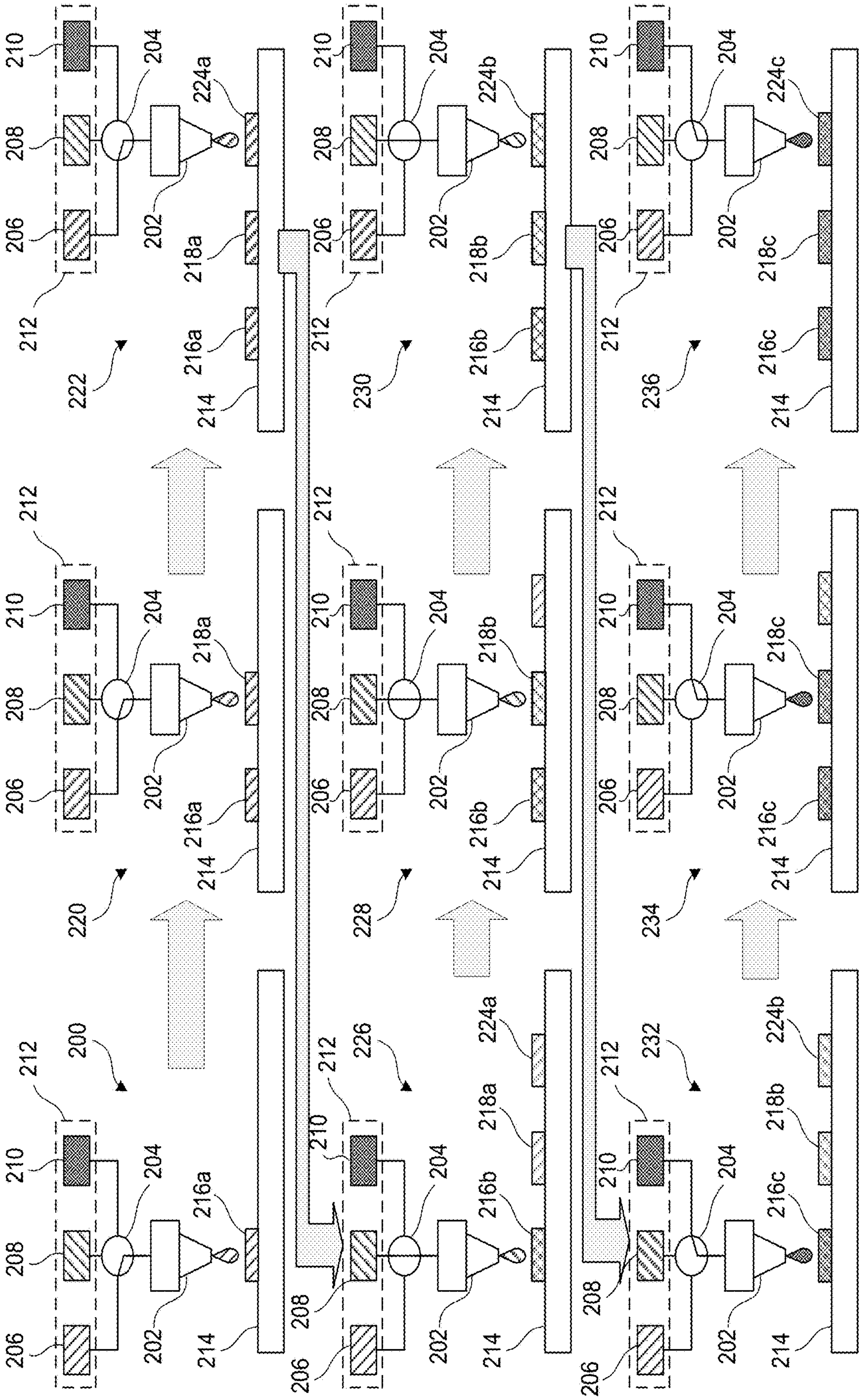
Probe
138
Actuator
140
Support
118
Control
148
I/O
Control
144
142
146

FIG. 1B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216c
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224b
214
234
212
210
208
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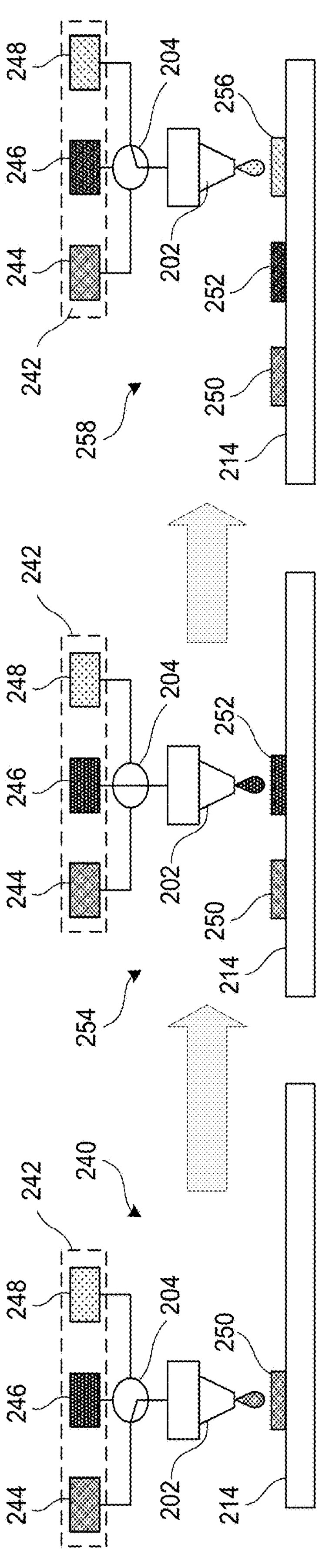
218c
216c
214

FIG. 2A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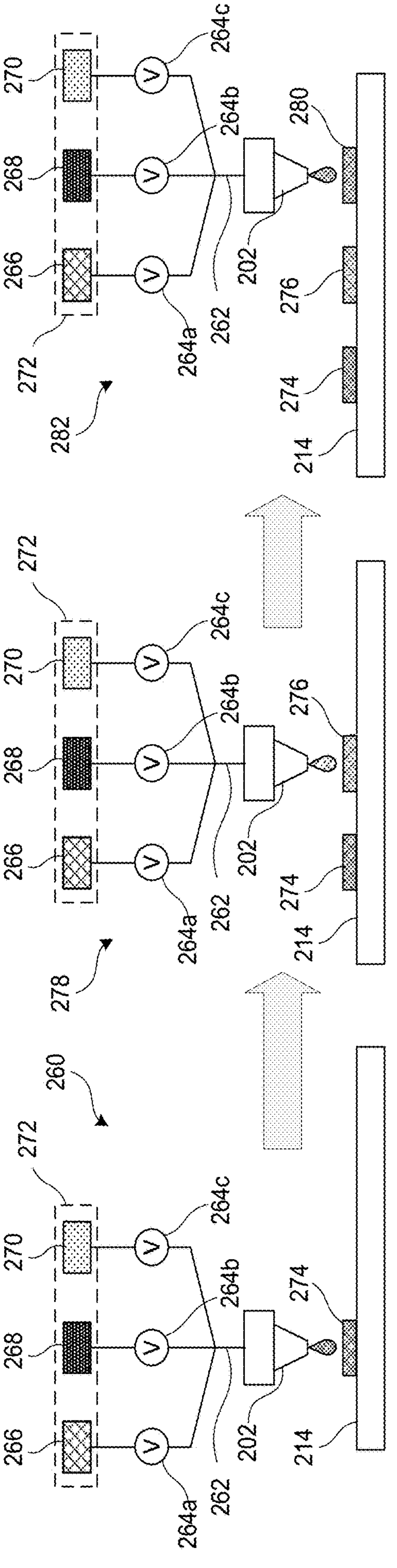
258
256

FIG. 2B


260
262
264a
264b
264c
V
266
268
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272
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214
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282

FIG. 2C

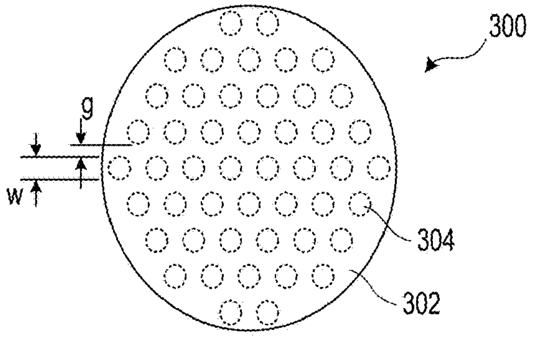

FIG. 3A

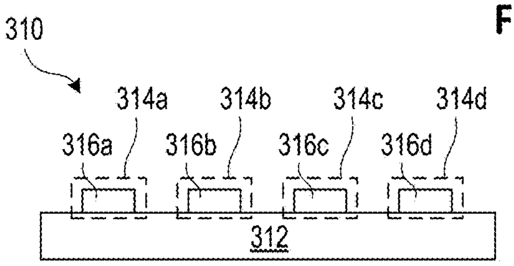

FIG. 3B

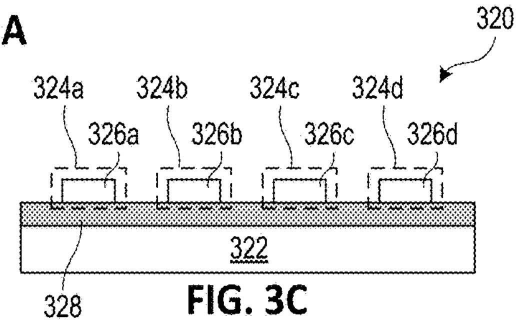

FIG. 3C

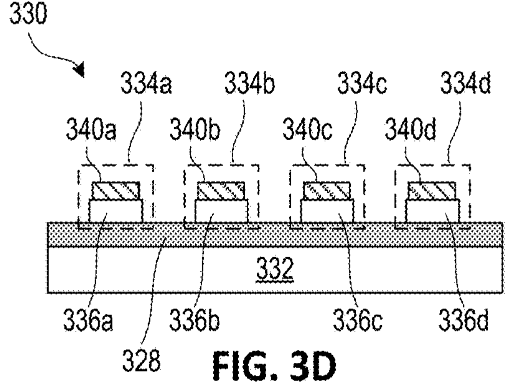

FIG. 3D

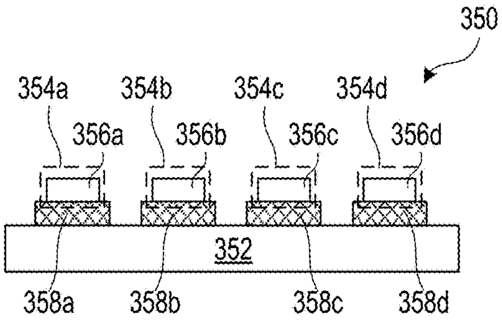

FIG. 3E

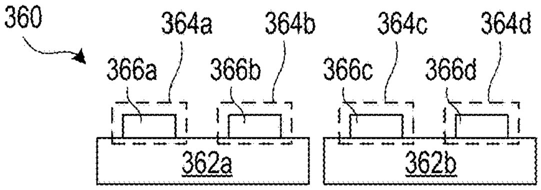

FIG. 3F

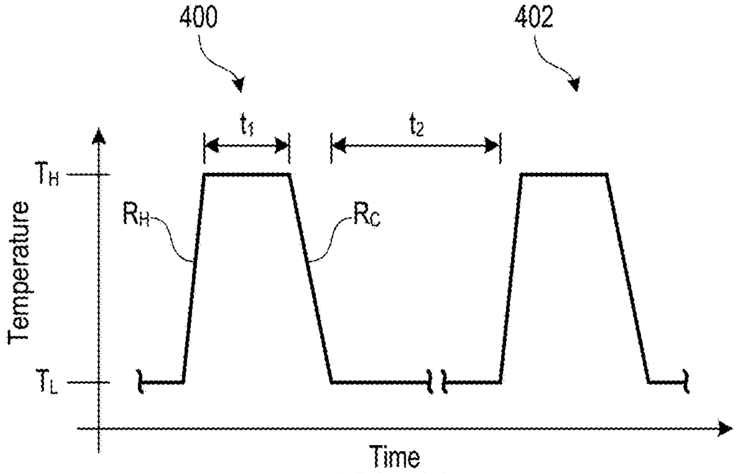

FIG. 4A

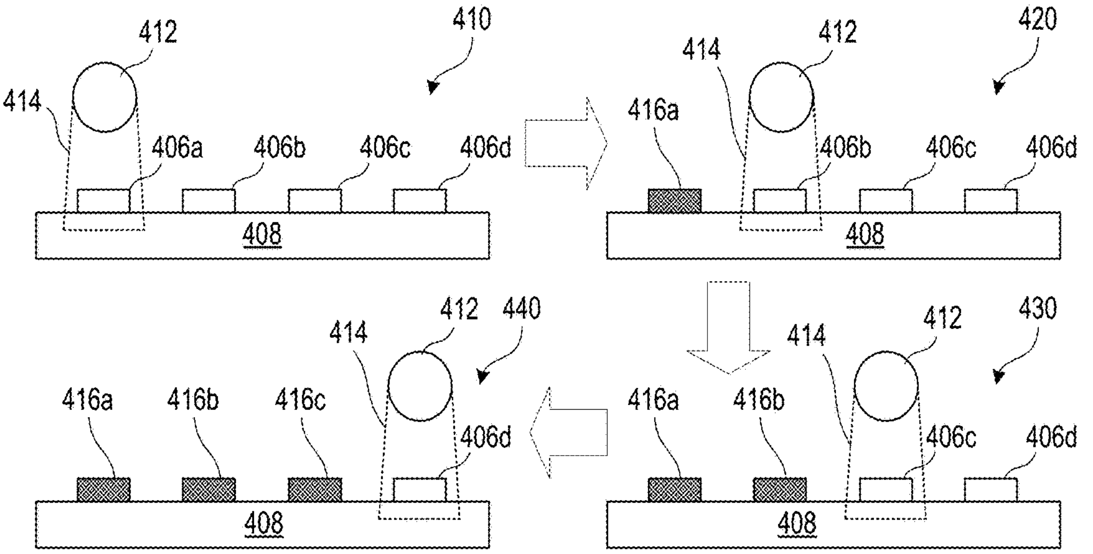

FIG. 4B

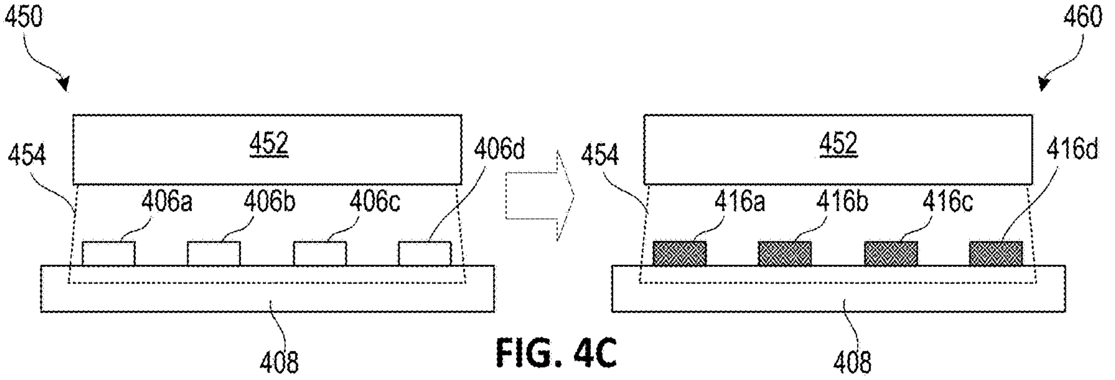

FIG. 4C

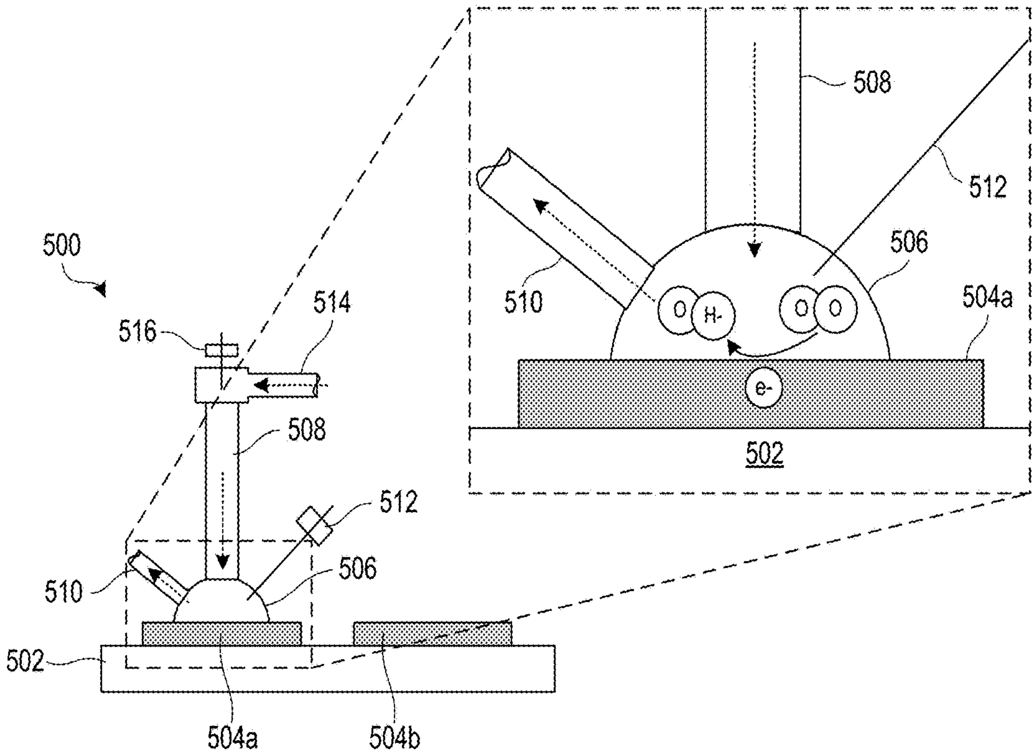

FIG. 5A

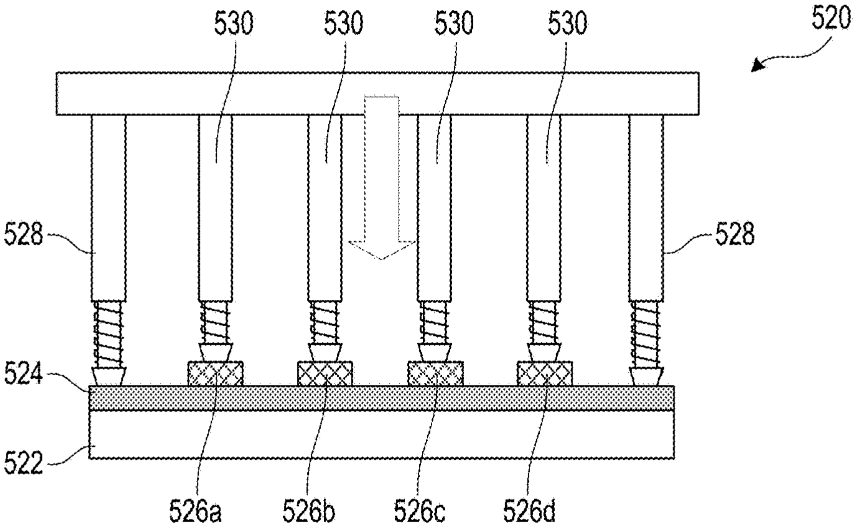

FIG. 5B

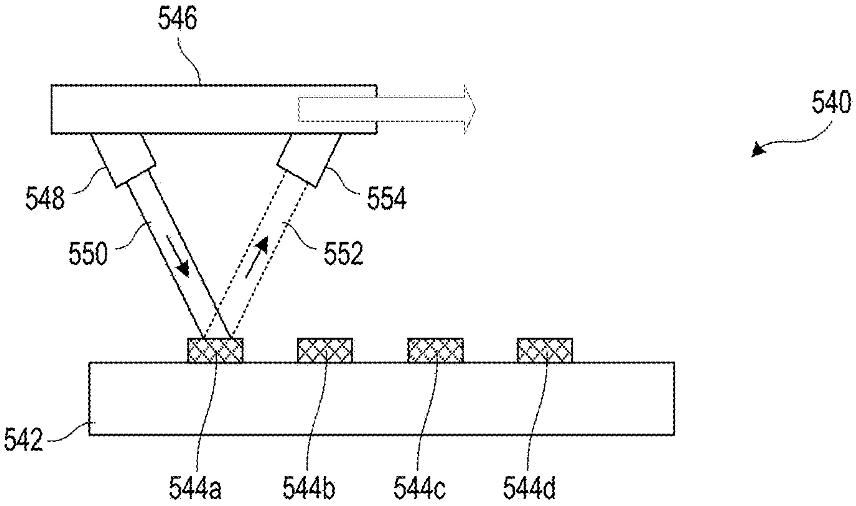

FIG. 5C

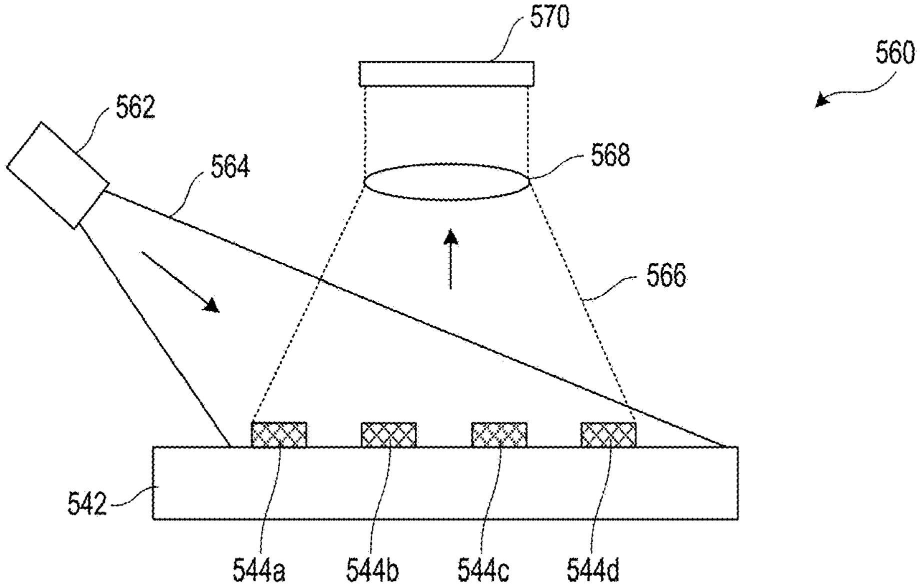

FIG. 5D

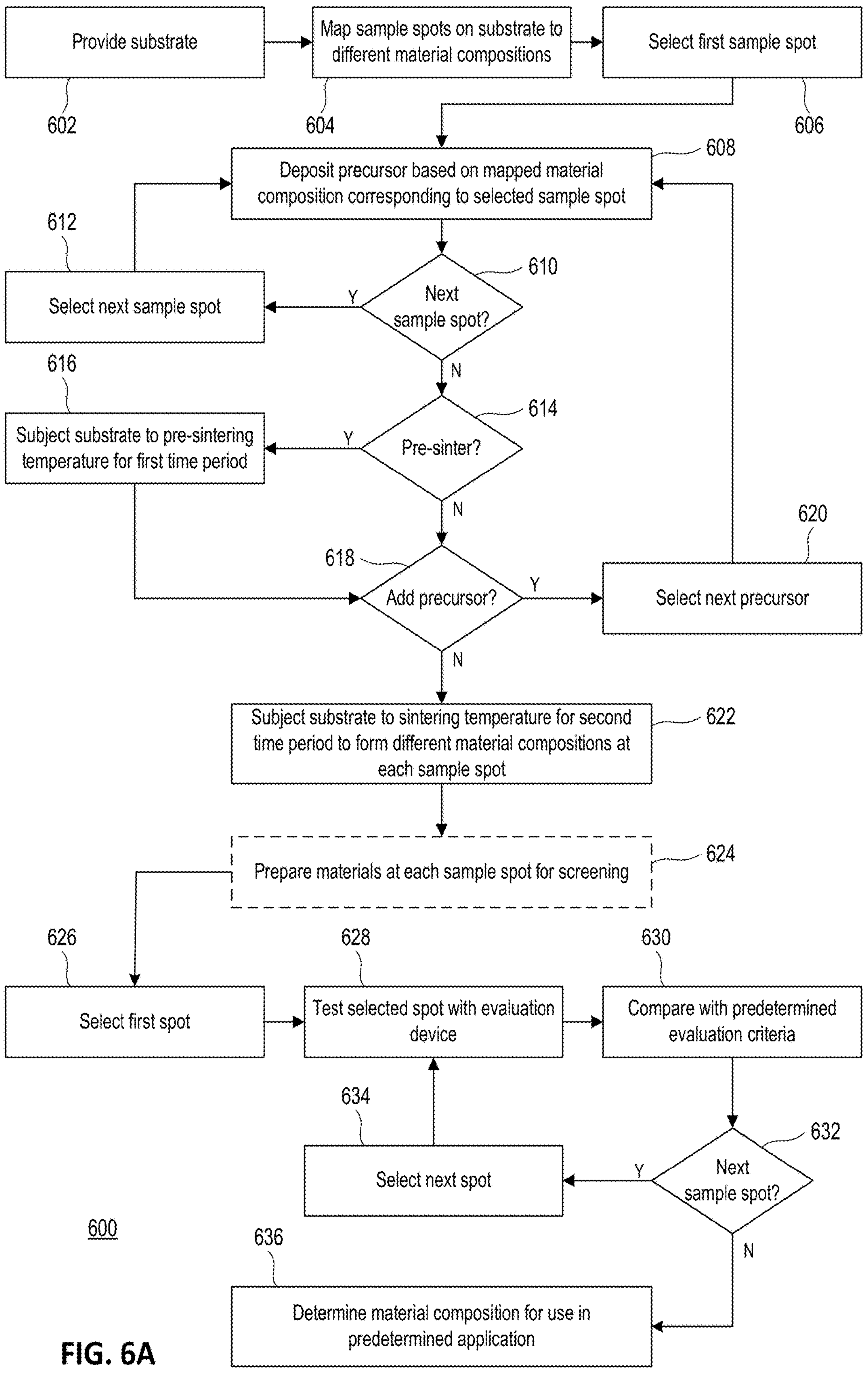
Provide substrate
602
Map sample spots on substrate to different material compositions
604
Select first sample spot
606
Deposit precursor based on mapped material composition corresponding to selected sample spot
608
612
Select next sample spot
Y
Next sample spot?
610
N
616
Subject substrate to pre-sintering temperature for first time period
Y
Pre-sinter?
614
N
618
Add precursor?
Y
620
Select next precursor
N
Subject substrate to sintering temperature for second time period to form different material compositions at each sample spot
622
Prepare materials at each sample spot for screening
624
626
Select first spot
628
Test selected spot with evaluation device
630
Compare with predetermined evaluation criteria
634
Select next spot
Y
Next sample spot?
632
N
600
636
Determine material composition for use in predetermined application

FIG. 6A

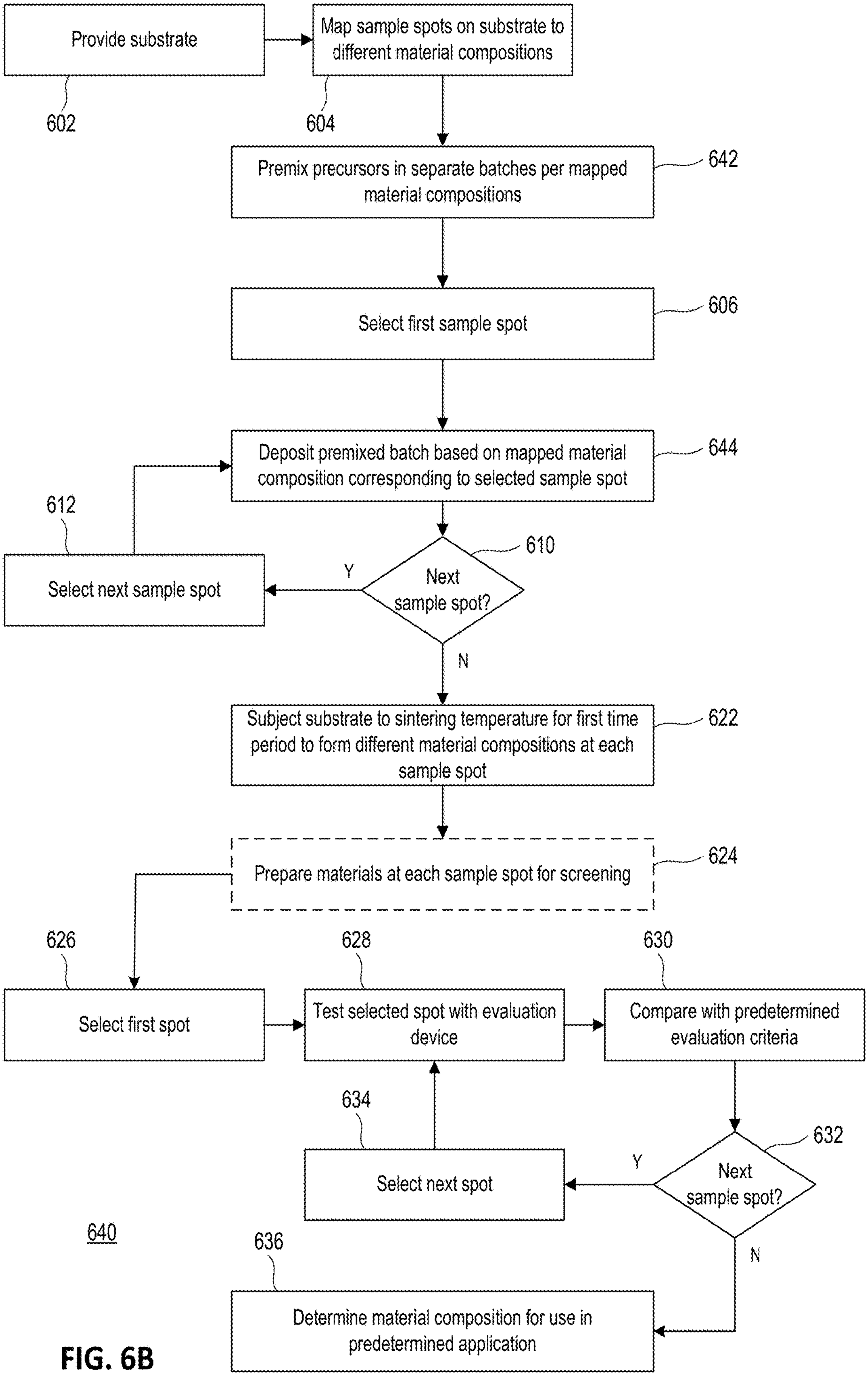
Provide substrate
602
Map sample spots on substrate to different material compositions
604
Premix precursors in separate batches per mapped material compositions
642
Select first sample spot
606
Deposit premixed batch based on mapped material composition corresponding to selected sample spot
644
612
Select next sample spot
Y
Next sample spot?
610
N
Subject substrate to sintering temperature for first time period to form different material compositions at each sample spot
622
Prepare materials at each sample spot for screening
624
626
628
630
Select first spot
Test selected spot with evaluation device
Compare with predetermined evaluation criteria
634
Select next spot
Y
Next sample spot?
632
N
640
636
Determine material composition for use in predetermined application

FIG. 6B

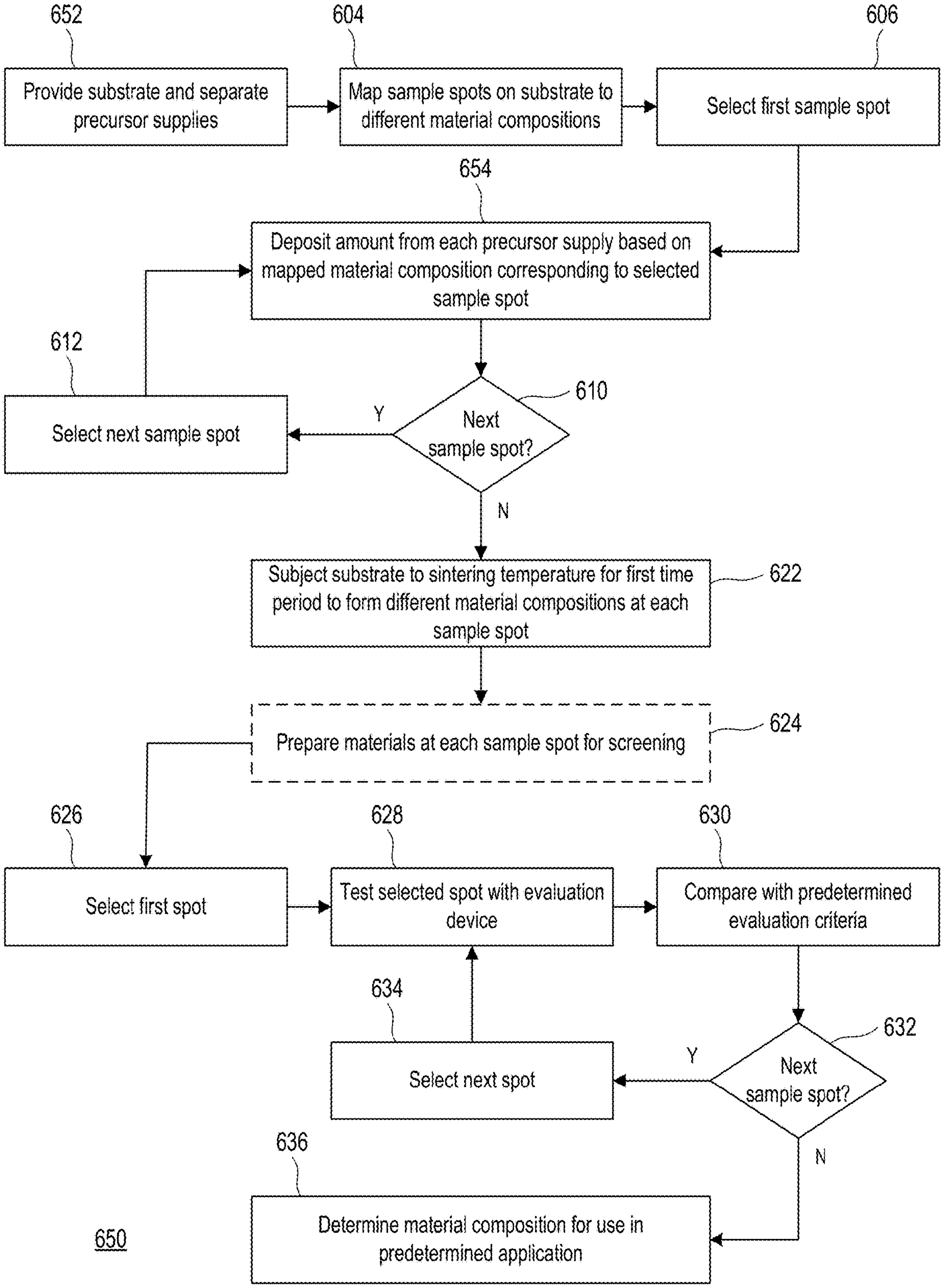
652
Provide substrate and separate precursor supplies
604
Map sample spots on substrate to different material compositions
606
Select first sample spot
654
Deposit amount from each precursor supply based on mapped material composition corresponding to selected sample spot
612
Select next sample spot
Y
610
Next sample spot?
N
Subject substrate to sintering temperature for first time period to form different material compositions at each sample spot
622
Prepare materials at each sample spot for screening
624
626
Select first spot
628
Test selected spot with evaluation device
630
Compare with predetermined evaluation criteria
634
Select next spot
Y
632
Next sample spot?
N
636
Determine material composition for use in predetermined application
650

FIG. 6C

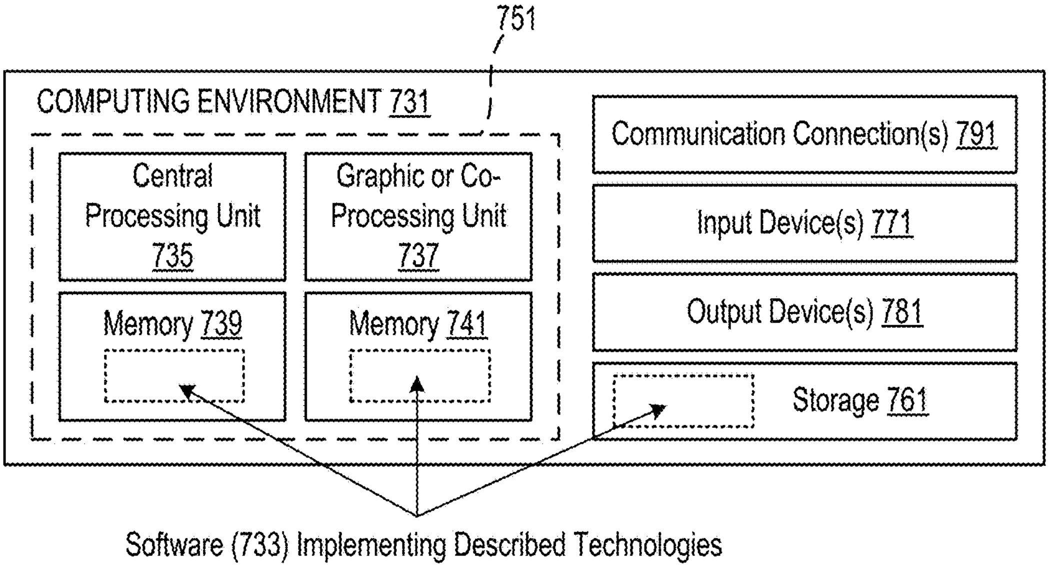

FIG. 7

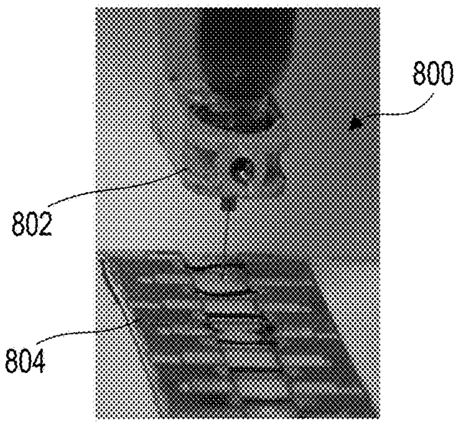

FIG. 8A

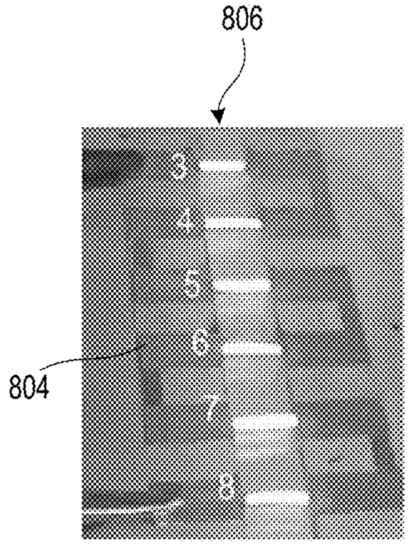

FIG. 8B

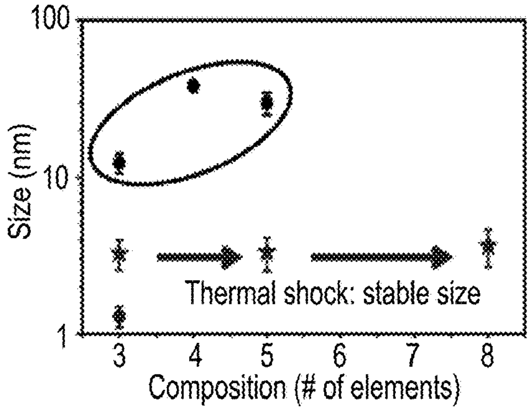

FIG. 9A

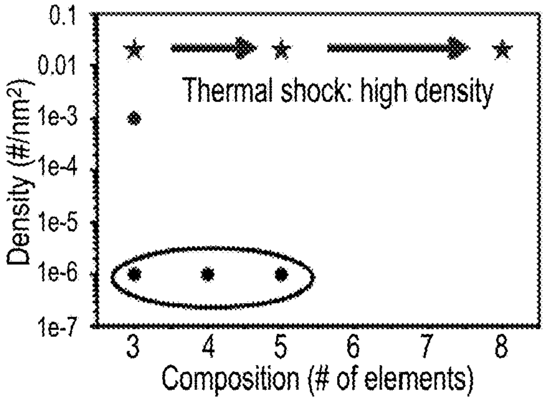

FIG. 9B

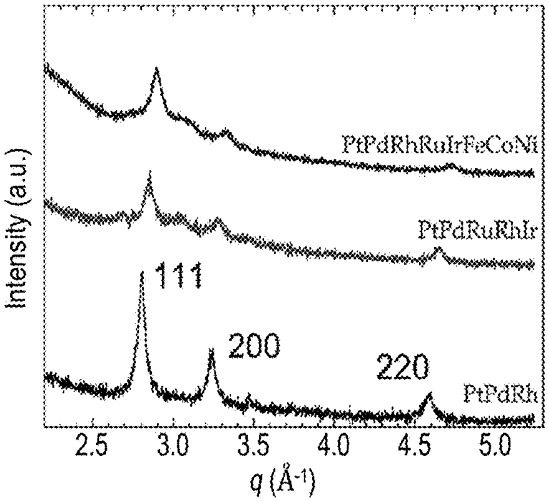

FIG. 10A

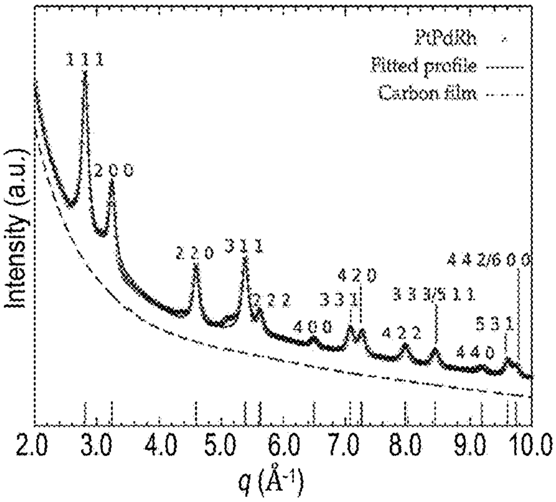

FIG. 10B

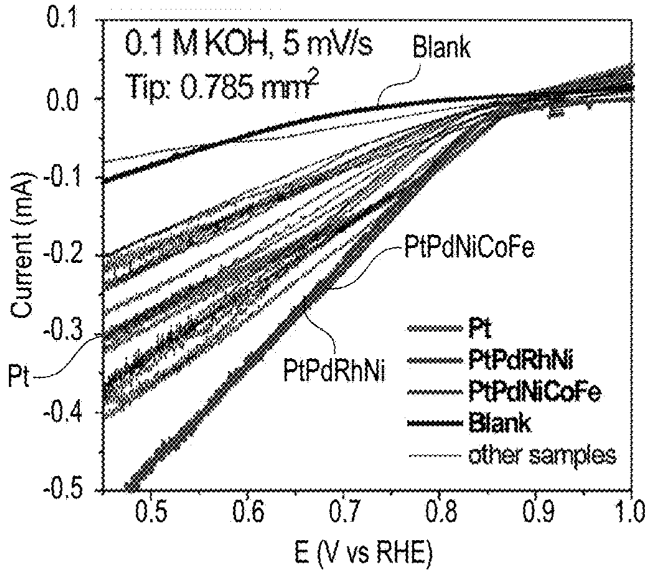

FIG. 11A

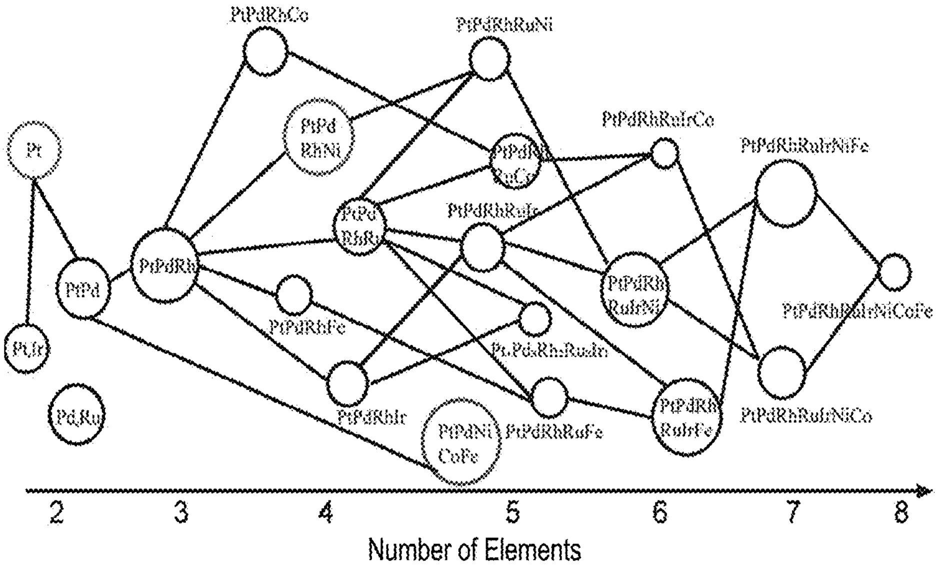

FIG. 11B

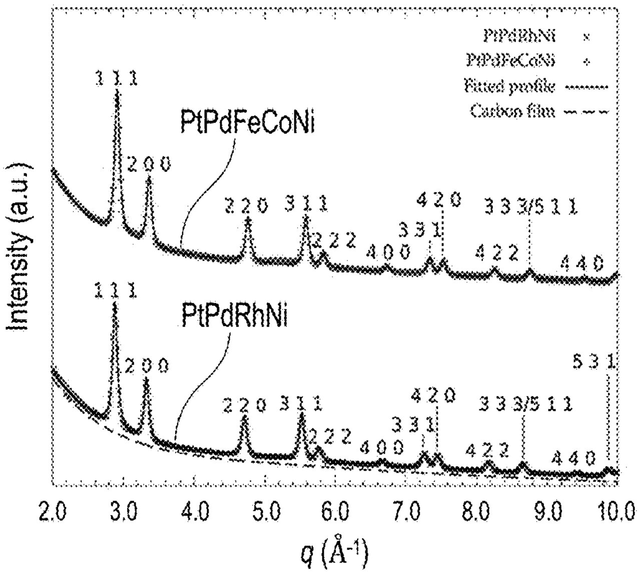

FIG. 11C

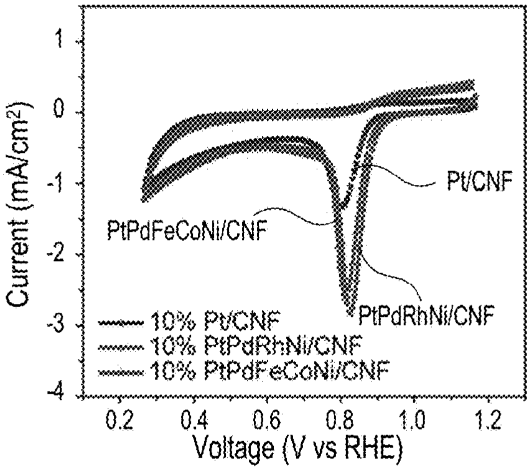

FIG. 12A

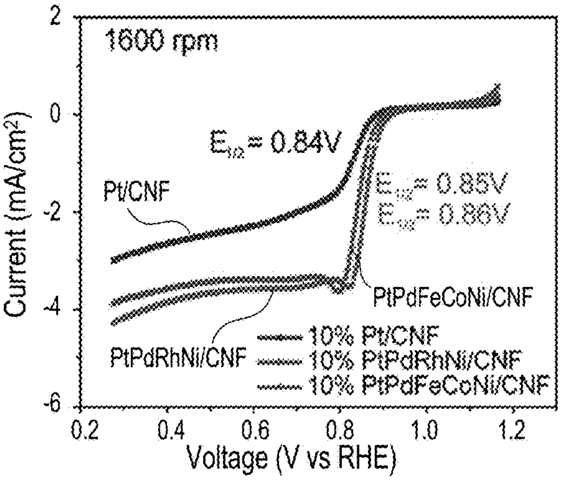

FIG. 12B

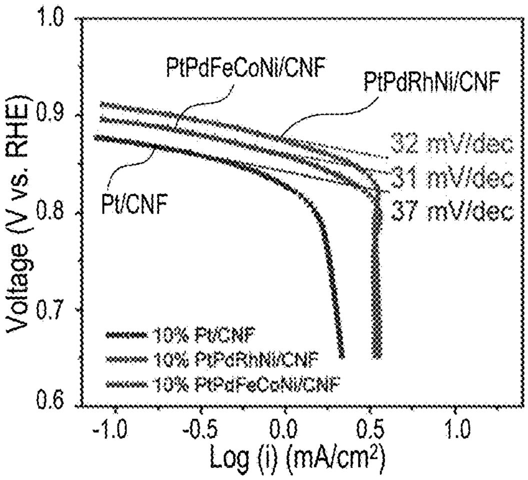

FIG. 12C

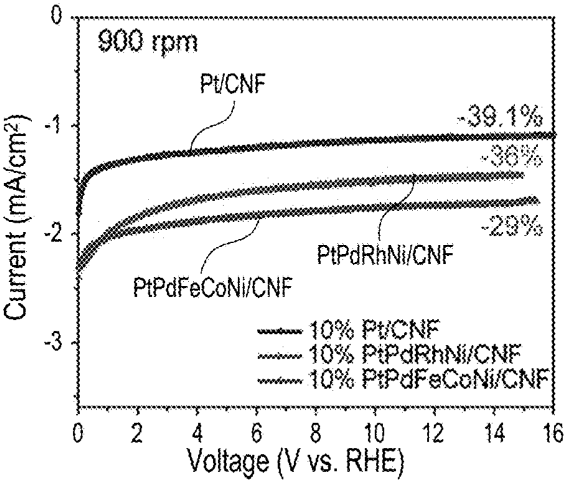

FIG. 12D

SYSTEMS AND METHODS FOR COMBINATORIAL SYNTHESIS AND SCREENING OF MULTIELEMENT MATERIALS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of U.S. Provisional Application No. 63/158,645, filed Mar. 9, 2021, entitled "Combinatorial Synthesis and High Throughput Screening of Multielement Nanoparticles and Functional Bulk Materials," which is incorporated by reference herein in its entirety.

FIELD

[0002] The present disclosure relates generally to multielement material synthesis, and more particularly, to systems and methods for determination of a composition of multielement material (e.g., nanocluster, nanoparticle, or bulk material) for a particular application via combinatorial synthesis and screening.

BACKGROUND

[0003] Nanoparticles with a range of sizes and morphologies have been studied for various catalytic applications. These nanoparticles are typically comprised of no more than three elements to avoid synthetic complexity and structural heterogeneity. Multielement nanoclusters having three or more elements thus present a vast and largely undiscovered chemical space that can offer synergistic interactions between different elements. Yet, with increasing compositional complexity, conventional fabrication methods can lead to multielement particles with large size distributions and/or inhomogeneous structures (e.g., phase separation and/or elemental segregation within the particles), which may result from the inability of conventional fabrication methods to control the kinetics and dynamics of chemical reactions at the nanoscale among dissimilar constituent elements. As a result, it remains a challenge to tune the composition of fabricated materials in order to systematically study the properties thereof, thus limiting material discovery, property optimization, and mechanistic understanding for different functionalities.

[0004] Embodiments of the disclosed subject matter may address one or more of the above-noted problems and disadvantages, among other things.

SUMMARY

[0005] Embodiments of the disclosed subject matter system provide systems and methods for combinatorial synthesis and screening of multielement materials, for example, multielement nanoclusters, nanoparticles, or bulk materials. Multielement nanomaterials hold great promise for various applications due to their widely tunable surface chemistries. Yet it remains challenging to efficiently study this multidimensional space because conventional approaches are typically slow and depend on serendipity. Embodiments of the disclosed subject matter can thus address these deficiencies by offering a high-throughput technique for combinatorial compositional design (e.g., formulation in solution phases) and rapid synthesis (e.g., rapid, high-temperature exposure on the order of seconds) of multielement (e.g., multimetallic) materials (e.g., nanoparticles, nanoclusters, and/or bulk materials) with a homogeneous structure. The materials with different compositions can be subject to rapid screening, for example, to discover optimal and/or synergistic compositions for particular applications, such as but not limited to use as a catalyst, a plasmonic nanoparticle, an energy storage device, an optoelectronic device, a solid-state electrolyte, an ion conductive membrane, a fluorescent material, a component thereof, or any combination of the foregoing.

[0006] In one or more embodiments, a method can comprise depositing one or more first precursors on a first portion of a substrate and depositing one or more second precursors on a second portion of the substrate. The second portion can be spaced from the first portion. The method can further comprise subjecting each of the first and second portions of the substrate to a first temperature for a first time period so as to convert the deposited one or more first precursors into a first material and to convert the deposited one or more second precursors into a second material. The first material can have a different composition than the second material. The first temperature can be greater than or equal to about 500° C., and a duration of the first time period can be less than about 60 seconds. In some embodiments, the method can further comprise testing each of the first and second materials with respect to an electrical property, a chemical property, an optical property, or any combination thereof. In some embodiments, the method can also comprise determining a composition of a material for use in a predetermined application based at least in part on results of the testing.

[0007] In one or more embodiments, a system can comprise a dispensing device, a heating device, and a control system. The dispensing device can have a nozzle facing a surface of a substrate and constructed to deposit precursors onto the substrate. At least one of the nozzle and the substrate can be movable with respect to the other. The heating device can be constructed to generate a first temperature of at least 500° C. The control system can be operatively coupled to the dispensing device and the heating device. The control system can comprise one or more processors and computer readable storage media. The computer readable storage media can store instructions that, when executed by the one or more processors, cause the control system to (i) control the dispensing device to position the nozzle with respect to a first portion of the substrate, (ii) deposit, via the nozzle, one or more first precursors on the first portion, (iii) control the dispensing device to position the nozzle with respect to a second portion of the substrate, the second portion being spaced from the first portion, (iv) deposit, via the nozzle, one or more second precursors on the second portion, and (v) subject, via the heating device, each of the first and second portions of the substrate to the first temperature for a first time period so to convert the deposited one or more first precursors into a first material and to convert the deposited one or more second precursors into a second material. The first material can have a different composition than the second material, and a duration of the first time period can be less than 60 seconds.

[0008] Any of the various innovations of this disclosure can be used in combination or separately. This summary is provided to introduce a selection of concepts in a simplified form that are further described below in the detailed description. This summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used to limit the scope of the claimed subject matter. The foregoing and other objects, features, and advantages of the disclosed technology will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Embodiments will hereinafter be described with reference to the accompanying drawings, which have not necessarily been drawn to scale. Where applicable, some elements may be simplified or otherwise not illustrated in order to assist in the illustration and description of underlying features. Throughout the figures, like reference numerals denote like elements.

[0010] FIG. **1**A is a simplified schematic diagram illustrating aspects of an exemplary synthesis system, according to one or more embodiments of the disclosed subject matter.

[0011] FIG. **1**B is a simplified schematic diagram illustrating aspects of exemplary synthesis and screening systems, according to one or more embodiments of the disclosed subject matter.

[0012] FIG. **2**A is a simplified schematic diagram illustrating operation of an exemplary dispensing device to sequentially deposit precursors, according to one or more embodiments of the disclosed subject matter.

[0013] FIG. **2**B is a simplified schematic diagram illustrating operation of another exemplary dispensing device to deposit pre-mixed samples, according to one or more embodiments of the disclosed subject matter.

[0014] FIG. **2**C is a simplified schematic diagram illustrating operation of another exemplary dispensing device to mix precursors and deposit samples, according to one or more embodiments of the disclosed subject matter.

[0015] FIG. **3**A is a plan view of an exemplary substrate with sample spot mapping, according to one or more embodiments of the disclosed subject matter.

[0016] FIG. **3**B is a simplified cross-sectional view of an exemplary substrate with samples deposited thereon, according to one or more embodiments of the disclosed subject matter.

[0017] FIG. **3**C is a simplified cross-sectional view of an exemplary substrate having an intervening layer with samples deposited thereon, according to one or more embodiments of the disclosed subject matter.

[0018] FIG. **3**D is a simplified cross-sectional view of an exemplary substrate having an intervening layer with samples deposited thereon and individual top electrodes, according to one or more embodiments of the disclosed subject matter.

[0019] FIG. **3**E is a simplified cross-sectional view of an exemplary substrate having individual sample deposition supports, according to one or more embodiments of the disclosed subject matter.

[0020] FIG. **3**F is a simplified cross-sectional view of an exemplary setup with multiple substrates having samples deposited thereon, according to one or more embodiments of the disclosed subject matter.

[0021] FIG. **4**A is a graph of an exemplary temperature profile for a heating element, according to one or more embodiments of the disclosed subject matter.

[0022] FIG. **4**B is a simplified cross-sectional view illustrating operation of sequential sintering of sample spots on a substrate, according to one or more embodiments of the disclosed subject matter.

[0023] FIG. **4**C is a simplified cross-sectional view illustrating operation of parallel sintering of sample spots on a substrate, according to one or more embodiments of the disclosed subject matter.

[0024] FIG. **5**A illustrates an exemplary evaluation device employing a scanning probe cell, according to one or more embodiments of the disclosed subject matter.

[0025] FIG. **5**B illustrates an exemplary evaluation device employing a plurality of pogo pins, according to one or more embodiments of the disclosed subject matter.

[0026] FIG. **5**C illustrates an exemplary evaluation device employing sequential optical irradiation and detection, according to one or more embodiments of the disclosed subject matter.

[0027] FIG. **5**D illustrates an exemplary evaluation device employing parallel optical irradiation and detection, according to one or more embodiments of the disclosed subject matter.

[0028] FIG. **6**A is a process flow diagram of an exemplary method for material synthesis and screening via sequential deposition of precursors, according to one or more embodiments of the disclosed subject matter.

[0029] FIG. **6**B is a process flow diagram of an exemplary method for material synthesis and screening via deposition of premixed precursors, according to one or more embodiments of the disclosed subject matter.

[0030] FIG. **6**C is a process flow diagram of an exemplary method for material synthesis and screening via simultaneous deposition of different precursors, according to one or more embodiments of the disclosed subject matter.

[0031] FIG. **7** depicts a generalized example of a computing environment in which the disclosed technologies may be implemented.

[0032] FIG. **8**A is an image of a printing nozzle depositing liquid phase precursors on a carbon support in a fabricated example.

[0033] FIG. **8**B is an image of thermal shock synthesis (~1650K, 500 ms) of the liquid phase precursors on the carbon support in a fabricated example.

[0034] FIGS. **9**A-**9**B are graphs of particle size and dispersal density, respectively, of multimetallic nanoclusters formed by the thermal shock of FIG. **8**B as compared to other synthesis techniques (circled).

[0035] FIG. **10**A is a graph of X-ray powder diffraction (XRD) measurements for ternary, quinary, and octonary MMNCs.

[0036] FIG. **10**B shows the synchrotron XRD (λ=0.2113 Å) profile of a fabricated MMNC of PtPdRh.

[0037] FIG. **11**A is a graph illustrating screening of PtPd-based MMNCs for catalytic oxygen reduction reaction (ORR) (22 compositions+1 blank, 0.1 M KOH, 5 mV/s scan rate).

[0038] FIG. **11**B illustrates a neural network diagram for compositional designs and their corresponding ORR performances, with circle size representing magnitude of the specific current at 0.45 V for ORR.

[0039] FIG. **11**C shows the synchrotron XRD profiles for PtPdRhNi and PtPdFeCoNi.

[0040] FIG. **12**A shows a cycle voltammogram of three fabricated MMNC samples for ORR.

[0041] FIG. **12**B shows a linear sweep voltammogram of the three fabricated MMNC samples of FIG. **12**A.

[0042] FIG. **12**C shows a Tafel analysis of the three fabricated MMNC samples of FIG. **12**A.

[0043] FIG. **12**D shows the results of a stability test for the three fabricated MMNC samples of FIG. **12**A.

DETAILED DESCRIPTION

General Considerations

[0044] For purposes of this description, certain aspects, advantages, and novel features of the embodiments of this disclosure are described herein. The disclosed methods and systems should not be construed as being limiting in any way. Instead, the present disclosure is directed toward all novel and nonobvious features and aspects of the various disclosed embodiments, alone and in various combinations and sub-combinations with one another. The methods and systems are not limited to any specific aspect or feature or combination thereof, nor do the disclosed embodiments require that any one or more specific advantages be present, or problems be solved. The technologies from any embodiment or example can be combined with the technologies described in any one or more of the other embodiments or examples. In view of the many possible embodiments to which the principles of the disclosed technology may be applied, it should be recognized that the illustrated embodiments are exemplary only and should not be taken as limiting the scope of the disclosed technology.

[0045] Although the operations of some of the disclosed methods are described in a particular, sequential order for convenient presentation, it should be understood that this manner of description encompasses rearrangement, unless a particular ordering is required by specific language set forth below. For example, operations described sequentially may in some cases be rearranged or performed concurrently. Moreover, for the sake of simplicity, the attached figures may not show the various ways in which the disclosed methods can be used in conjunction with other methods. Additionally, the description sometimes uses terms like "provide" or "achieve" to describe the disclosed methods. These terms are high-level abstractions of the actual operations that are performed. The actual operations that correspond to these terms may vary depending on the particular implementation and are readily discernible by one skilled in the art.

[0046] The disclosure of numerical ranges should be understood as referring to each discrete point within the range, inclusive of endpoints, unless otherwise noted. Unless otherwise indicated, all numbers expressing quantities of components, molecular weights, percentages, temperatures, times, and so forth, as used in the specification or claims are to be understood as being modified by the term "about." Accordingly, unless otherwise implicitly or explicitly indicated, or unless the context is properly understood by a person skilled in the art to have a more definitive construction, the numerical parameters set forth are approximations that may depend on the desired properties sought and/or limits of detection under standard test conditions/methods, as known to those skilled in the art. When directly and explicitly distinguishing embodiments from discussed prior art, the embodiment numbers are not approximates unless the word "about" is recited. Whenever "substantially," "approximately," "about," or similar language is explicitly used in combination with a specific value, variations up to and including 10% of that value are intended, unless explicitly stated otherwise.

[0047] Directions and other relative references may be used to facilitate discussion of the drawings and principles herein, but are not intended to be limiting. For example, certain terms may be used such as "inner," "outer,", "upper," "lower," "top," "bottom," "interior," "exterior," "left," right," "front," "back," "rear," and the like. Such terms are used, where applicable, to provide some clarity of description when dealing with relative relationships, particularly with respect to the illustrated embodiments. Such terms are not, however, intended to imply absolute relationships, positions, and/or orientations. For example, with respect to an object, an "upper" part can become a "lower" part simply by turning the object over. Nevertheless, it is still the same part and the object remains the same.

[0048] As used herein, "comprising" means "including," and the singular forms "a" or "an" or "the" include plural references unless the context clearly dictates otherwise. The term "or" refers to a single element of stated alternative elements or a combination of two or more elements, unless the context clearly indicates otherwise.

[0049] Although there are alternatives for various components, parameters, operating conditions, etc. set forth herein, that does not mean that those alternatives are necessarily equivalent and/or perform equally well. Nor does it mean that the alternatives are listed in a preferred order, unless stated otherwise. Unless stated otherwise, any of the groups defined below can be substituted or unsubstituted.

[0050] Unless explained otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one skilled in the art to which this disclosure belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present disclosure, suitable methods and materials are described below. The materials, methods, and examples are illustrative only and not intended to be limiting. Features of the presently disclosed subject matter will be apparent from the following detailed description and the appended claims.

Overview of Terms

[0051] The following explanations of specific terms and abbreviations are provided to facilitate the description of various aspects of the disclosed subject matter and to guide those skilled in the art in the practice of the disclosed subject matter.

[0052] Thermal shock: Application of a sintering temperature for a time period having a duration less than about 60 seconds. In some embodiments, the duration of the time period of sintering temperature application is in a range of about 0.5 seconds to about 30 seconds, inclusive.

[0053] Sintering temperature: A maximum temperature at a surface of a heating element when energized (e.g., by application of a current pulse). In some embodiments, the sintering temperature is at least about 500° C., for example, in a range of about 1000 to about 3000° C. In some embodiments, a temperature at a material being sintered (e.g., precursors on a substrate) within the furnace can match or substantially match (e.g., within 10%) the temperature of the heating element.

[0054] Particle size: A maximum cross-sectional dimension (e.g., diameter) of particle. In some embodiments, an identified particle size represents an average particle size for all particles in a particular sample (e.g., an average of the maximum cross-sectional dimensions).

[0055] Nanoparticle: A particle composed of at least two different elements and having a particle size less than or equal to about 1 μm. In some embodiments, each nanoparticle has a size of about 100 nm or less, for example, about 25 nm or less.

[0056] Nanocluster: A particle composed of at least two different elements and having a particle size less than or equal to about 2 nm.

[0057] Bulk material: A material composed of at least two different elements and having at least one dimension greater than or equal to about 1 mm.

[0058] Precursor: One or more materials that, when subjected to thermal shock, are converted to a nanoparticle, nanocluster, or bulk material. In some embodiments, the precursors can comprise metal salts and/or metal oxides that, when subjected to thermal shock, are converted to a homogeneous mixture of metals. Alternatively or additionally, the precursors can be converted via thermal shock to a ceramic (e.g., oxide, nitride, etc.), carbon, heterogeneous or hybrid structure, composite, metal, or any combination of the foregoing.

[0059] Refractory material: A material (e.g., element or compound) having a melting temperature of at least 1000° C., for example, at least 1580° C. In some embodiments, a refractory material can be as defined in ASTM C71-01, "Standard Terminology Relating to Refractories," August 2017, which is incorporated herein by reference.

[0060] Refractory metal: A metal or metal alloy having a melting point of at least 1000° C., for example, at least 1850° C. In some embodiments, a refractory metal is one of niobium, molybdenum, tantalum, tungsten, rhenium, or an alloy thereof.

[0061] Metal: Includes those individual chemical elements classified as metals on the periodic table, including alkali metals, alkaline earth metals, transition metals, lanthanides, and actinides, as well as alloys formed from such metals, such as, but not limited to, stainless steel, brass, bronze, monel, etc.

Introduction

[0062] In one or more embodiments, a combinatorial approach can provide parallel (or pseudo-parallel) synthesis of a large number (e.g., tens, hundreds, thousands, etc.) of samples of different material compositions comprised of multiple elements (e.g., at least two, such as three or more), thereby saving tremendous time and effort. In some embodiments, all of the samples (or at least a subset thereof) can be provided on a common substrate, for example, for part of the synthesis process (e.g., simultaneous or sequential thermal shock of each sample spot on the substrate) and/or subsequent screening (e.g., simultaneous or sequential testing of each sample spot on the substrate). After synthesis, high throughput screening can rapidly acquire data indicative of one or more properties of these compositionally different multielement materials (e.g., nanoparticles, nanoclusters, or functional bulk materials). By combining combinatorial synthesis and high throughput screening, rapid material discovery and exploration in new multielement dimensions becomes possible.

[0063] One or more embodiments can include (a) multielement composition design, (b) a combinatorial precursor mapping for a large number (e.g., at least 20, at least 50, at least 100, or at least 1000) of different compositions, (c) thermal shock heating that synthesizes materials with similar structures (e.g., particle size, particle dispersion density, single phase, homogeneous distribution, etc.) despite otherwise different compositions; and (d) high throughput screening of compositionally different samples with respect to targeted properties. In some embodiments, the multielement composition design can comprise selection of particular elements for combination (e.g., from a subset of Pt, Pd, Rh, Ru, Ir, Fe, Co, Au, Mn, and Ni) and/or selection of number of elements per particle (e.g., three elements per particle) or a range of number of elements per particle (e.g., in a range of three to eight elements per particle).

[0064] In some embodiments, the combinatorial precursor mapping can include varying element compositions in a spatial arrangement (e.g., composition of one element varying in a stepwise gradual manner along one linear dimension, for example, an element composition for a plurality of samples varying from 1% at one end of the substrate to 99% at an opposite end of the substrate in increments of 1%) or any other predetermined manner. For example, the mapping can utilize a mathematical object in which all possible combinations of elements are covered at least once, similar to a covering array. Alternatively or additionally, a combinatorial algorithm, such as group testing algorithms, can be employed to determine variations of element compositions of the multielement materials for analysis, either formed on a common substrate or spread across multiple substrates.

[0065] In some embodiments, the thermal shock heating can be performed on multiple sample spots at time, for example, to simultaneously form multielement materials on the substrate having different material compositions for analysis. For example, the systems and methods for thermal shock heating and/or the multielement materials formed by thermal shock heating can be similar to those disclosed in U.S. Publication No. 2018/0369771, entitled "Nanoparticles and systems and methods for synthesizing nanoparticles through thermal shock," U.S. Publication No. 2019/0161840, entitled "Thermal shock synthesis of multielement nanoparticles," International Publication No. WO 2020/236767, entitled "High temperature sintering systems and methods," and International Publication No. WO 2020/252435, entitled "Systems and methods for high temperature synthesis of single atom dispersions and multi-atom dispersions," all of which are incorporated by reference herein.

[0066] In some embodiments, the high throughput screening can evaluate the plurality of multielement samples on the substrate with respect to one or more properties, such as but not limited to electrical properties (e.g., conductivity, resistance, impedance, etc.), chemical properties (e.g., catalytic or electrocatalytic effect, electrochemical impedance, etc.), optical property (e.g., plasmonic effect, fluorescence, etc.), or any combination thereof. In some embodiments, the high throughput screening can interrogate and evaluate each multielement sample spot on the substrate individually, for example, in a sequential manner. Alternatively or additionally, in some embodiments, the high throughput screening can interrogate and evaluate each multielement sample spot on the substrate collectively, for example, in a parallel manner.

[0067] Some embodiments can further include (e) integrating feedback from the screening to direct selection of multielement compositions for further combinatorial synthesis and screening (e.g., by repeating (a)-(d)). For example, once one or more samples are identified as potential options for the predetermined application during an initial iteration of the combinatorial synthesis and screening, a smaller region of diversity space around the one or more identified samples can be probed by a subsequent iteration of the combinatorial synthesis and screening to find improved or additional options. In some embodiments, the feedback can employ optimization algorithms (e.g., a genetic algorithm), data mining, and/or machine learning to determine sample compositions for further screening and/or use in the predetermined application. Some embodiments can further include (f) selection of one or more compositions based on the one or more screenings for use in the predetermined application. Such applications can include but are not limited to use as (i) a catalyst, (ii) a plasmonic nanoparticle, (iii) an energy storage device, (iv) an optoelectronic device, (v) a solid-state electrolyte, (vi) an ion conductive membrane, (vii) a fluorescent material, (viii) a component of any of (i)-(vii), or any combination of (i)-(viii).

Exemplary Multielement Material Synthesis and Screening Systems

[0068] FIG. 1A illustrates an exemplary synthesis system **102**. In the illustrated example, the synthesis system **102** can comprise a dispensing device **104** and a heating device **116**. The dispensing device **104** can comprise a supply of one or more precursors **106** and a dispensing nozzle **108**. The precursor supply **106** can include, for example, one or more reservoirs of salts or oxides (e.g., metal salts or oxides) in solution (e.g., organic solvent, such as ethanol, methanol, isopropyl alcohol (IPA), or acetone). In some embodiments, the concentration of precursors within the reservoirs can be at a level that allows dispensing from the nozzle as a liquid (e.g., a low density), for example, when formation of nanoclusters or nanoparticles is desired. Alternatively or additionally, in some embodiments, the concentration of precursors within the reservoirs can be higher (e.g., with less solution), such that the precursors are dispensed from the nozzle as an ink or slurry, for example, when formation of a bulk material is desired. Alternatively or additionally, in some embodiments, the precursors can be in various states, such as in a vapor state or microparticles.

[0069] In some embodiments, the dispensing device **104** can also include a support **112**, for example, a movable or stationary platform where a substrate can be disposed. The dispensing device **104** can further include one or more actuators **110**. In some embodiments, the actuator(s) **110** can be coupled to nozzle **108** to position the nozzle **108** with respect to the substrate. Alternatively or additionally, in some embodiments, the actuator(s) **110** can be coupled to support **112** to position the substrate with respect to the nozzle **108**. The actuator(s) **110** can thus provide motion in at least one dimension, for example, two dimensions parallel to a deposition surface of the substrate, or, in some embodiments, three dimensions (e.g., to change a vertical spacing between the nozzle **108** and the deposition surface of the substrate). In some embodiments, the dispensing device **104** can be an ink jet printhead, an additive manufacturing printhead (e.g., 3D printer), a robotic pipetting device, or any other mechanism for controlled dispensing of fluids (e.g., inks, suspensions, slurries, etc.).

[0070] The heating device **116** can be constructed to apply a thermal shock, for example, by providing a temperature in excess of 500° C. (e.g., in a range of 1000-3000° C., inclusive) for a time period less than 60 seconds (e.g., in a range of 0.5 to 30 seconds, inclusive). In some embodiments, the heating device **116** can comprise a Joule heating (e.g., with the heating element in contact with the precursors to provide conductive heating and/or spaced from the precursors to provide radiation heating), microwave heating, laser heating, plasma heating, or any combination thereof.

[0071] In some embodiments, the synthesis system **102** can include one or more transport mechanisms **120** to convey the substrate from the dispensing device **104** to the heating device **116**. Alternatively or additionally, the synthesis system **102** can include one or more transport mechanisms **122** to convey the substrate from the heating device **116**. In some embodiments, the transport mechanism **122** may be combined with and/or considered part of transport mechanism **120**. Alternatively, in some embodiments, transport mechanism **122** may be separate from and/or operate independently of transport mechanism **120**. For example, in some embodiments, the transport mechanism **120**, transport mechanism **122**, or both can comprise a conveyor system (e.g., comprising one or more belts and/or rollers). Alternatively or additionally, in some embodiments, either or both of the transport mechanisms **120**, **122** can comprise a pick-and-place robot, magnetic actuators, pneumatic or vacuum actuators, or any other transport mechanism.

[0072] Synthesis system **102** can further include a control sub-system **118**, which can be operatively coupled to the various components of synthesis system **102**, e.g., dispensing device **104**, heating device **116**, and/or transport mechanisms **120**, **122**, to direct operation thereof. For example, the control sub-system **118** can control the dispensing device **104** to dispense precursors at a plurality of sample spots on the substrate with different elemental compositions according to a combinatorial approach. After dispensing of the precursors, the control sub-system **118** can direct transport mechanism **120** to move the substrate to heating device **116** and to control the heating device **116** to generate a thermal shock. The thermal shock can be effective to convert the precursors at each sample spot **126** to a substantially homogeneous solid mixture of multiple elements (e.g., multielement material, such as multielement nanoparticle **128**). Since the precursors were loaded across the substrate **124** according to the combinatorial approach, each of the sample spots can have a different material composition. Despite the different material compositions, the thermal shock treatment can be effective to generate materials that otherwise have substantially similar particle sizes and uniformity, which features can be useful for subsequent screening and comparison of material properties.

[0073] The control sub-system **118** can direct transport mechanism **122** to move the substrate **124**, with sample spots having different material compositions thereon, from the heating device **116** for subsequent screening, for example, via a separate screening system or via an integrated screening system. For example, FIG. 1B illustrates an exemplary system **100** comprising synthesis system **102** and a screening system **132**. In the illustrated example, screening system **132** can comprise an evaluation device **134**. The evaluation device **134** can comprise a probe head **136**, for example, to make electrical, electrochemical, or mechanical contact with a particular sample spot or to otherwise interrogate (e.g., by directing optical radiation at) with a particular sample spot on the substrate. The evaluation device **134** can be configured to measure an electrical property, a chemical property, and/or an optical property of the interrogated sample spot.

[0074] In some embodiments, the evaluation device **134** can also include a support **140**, for example, a movable or stationary platform where the substrate can be disposed. The evaluation device **134** can further include one or more actuators **138**. In some embodiments, the actuator(s) **138** can be coupled to probe head **136** to position the probe head **136** with respect to the substrate. Alternatively or additionally, in some embodiments, the actuator(s) **138** can be coupled to support **140** to position the substrate with respect to the probe head **136**. The actuator(s) **138** can thus provide motion in at least one dimension, for example, two dimensions parallel to a deposition surface of the substrate, or, in some embodiments, three dimensions (e.g., to change a vertical spacing between the probe head **136** and the sample spots on the substrate). In some embodiments, the evaluation device **134** is configured to perform parallel testing of sample spots, for example, to interrogate multiple sample spots at once. For example, optical radiation can be directed at multiple spots on the substrate, and the multiple spots imaged simultaneously. Alternatively or additionally, in some embodiments, the evaluation device **134** operates in a serial manner, for example, by testing a single sample spot at a time.

[0075] Screening system **132** can further include a control sub-system **148**, which can be operatively coupled to the various components of screening system **132**, e.g., evaluation device **134**, input/output (I/O) interface **144**, and/or database **142**, to direct operation thereof. In some embodiments, control sub-system **148**, control sub-system **118**, I/O interface **144**, and/or database **142** can be considered part of a system-wide control system **146**. Alternatively, in some embodiments, control sub-system **148** and control sub-system **118** may be considered separate from each other, although in some cases the control sub-systems may communicate with each other, for example, to coordinate transfer of a substrate from synthesis system **102** and screening system **132** via transport mechanism **122**.

[0076] In some embodiments, the control sub-system **148** can control the evaluation device **134** to test one, some, or all of the sample spots on the substrate with respect to one or more material properties. The resulting data can be stored in database **142** for further processing. Alternatively or additionally, in some embodiments, the control sub-system **148** can be configured to analyze the data to determine an optimal material composition for a particular application. In some embodiments, the control sub-system **148** can provide feedback to synthesis system **102** (e.g., via communication with control sub-system **118**) regarding material compositions that should be further investigated in a subsequent combinatorial synthesis iteration, for example, by investigating material compositions in a vicinity of a highest scoring material from a prior combinatorial synthesis run. Alternatively or additionally, the control sub-system **148** can employ data mining techniques and/or machine learning (e.g., with or without consideration of data from prior combinatorial synthesis runs stored in database **142**) to identify material compositions that should be further investigated in a subsequent combinatorial synthesis iteration. Alternatively or additionally, the control sub-system **148** may simply select one of the tested sample spots from the substrate that has the best material properties for the particular application (or a set of test sample spots that have the top material properties). I/O interface **144** can be used to communicate results of the screening to a human user (e.g., via a graphical display) and/or to accept input from a human user (e.g., to direct material compositions of a subsequent combinatorial synthesis iteration and/or control system operations).

Exemplary Precursor Dispensing Devices

[0077] FIG. **2**A illustrates an exemplary operation for dispensing of precursors on substrate **214** via nozzle **202**. A supply **212** of multiple precursors can be fluidically coupled to the nozzle **202** via multi-position valve **204**. In the illustrated example, supply **212** has a first reservoir **206** for a first precursor, a second reservoir **208** for a second precursor, and a third reservoir **210** for a third precursor; however, the supply **212** can include any number of reservoirs, for example, corresponding to the number of different precursors required to form the different material combinations according to the combinatorial approach (e.g., three to eight precursors corresponding to three to eight elements in each multielement material). Indeed, the example of FIG. **2**A illustrates three precursors and corresponding deposited spots for simplicity only, but practical embodiments may include more than three precursors and more deposited spots (e.g., on the order of 10s, 100s, or even 1000s). Moreover, although the example of FIG. **2**A suggests deposition of precursor on each sample spot, embodiments of the disclosed subject matter are not limited thereto. Rather, a precursor can be applied to one, some, or all of the sample spots, depending on the details of the designed combinatorial approach.

[0078] At stage **200**, nozzle **202** can be aligned with a first spot location, for example, by moving nozzle **202** with respect to substrate **214**, by moving substrate **214** with respect to the nozzle **202**, or both. A predetermined first amount of first precursor (e.g., corresponding to a desired composition of the ultimate multielement material corresponding to the spot location) can be dispensed from first reservoir **206** to the first spot location via nozzle **202**, thereby forming first sample **216***a*. As shown at stage **220**, the nozzle **202** can then be aligned with a second spot location, for example, by moving the nozzle **202** and/or the substrate **214**, and a predetermined second amount of first precursor (which second amount may be different than that of the first precursor sample **216***a*) can be dispensed from first reservoir **206** to the second spot location via nozzle **202**, thereby forming second sample **218***a*. As shown at stage **222**, the nozzle **202** can then be aligned with a third spot location, for example, by moving the nozzle **202** and/or the substrate **214**, and a predetermined third amount of first precursor (which third amount may be different than that of first sample **216***a* and/or second sample **218***a*) can be dispensed from first reservoir **206** to the third spot location via nozzle **202**, thereby forming third sample **224***a*.

[0079] The nozzle **202** can then reconfigure for deposition of the second precursor on the same spot locations (e.g., thereby mixing the precursors in place on the substrate). For example, the valve **204** can switch orientations to couple the second reservoir **208** of supply **212** to nozzle **202**. At stage **226**, nozzle **202** can be re-aligned with the first spot location by moving the nozzle **202** and/or the substrate **214**, and a predetermined fourth amount of second precursor (e.g., corresponding to a desired composition of the ultimate multielement material corresponding to the spot location) can be dispensed from second reservoir **208** to the first spot location via nozzle **202**, thereby forming a first mixed sample **216***b* (e.g. formed of a first amount of first precursor and a fourth amount of second precursor). As shown at stage **228**, the nozzle **202** can then be re-aligned with the second spot location, for example, by moving the nozzle **202** and/or the substrate **214**, and a predetermined fifth amount of second precursor (which fifth amount may be different than the fourth amount of second precursor in sample **216***b*) can be dispensed from second reservoir **208** to the second spot location via nozzle **202**, thereby forming second mixed sample **218***b*. As shown at stage **230**, the nozzle **202** can then be re-aligned with the third spot location, for example, by moving the nozzle **202** and/or the substrate **214**, and a predetermined sixth amount of second precursor (which sixth amount may be different than the fourth amount of second precursor in sample **216***b* and/or the fifth amount of second precursor in sample **218***b*) can be dispensed from second reservoir **208** to the third spot location via nozzle **202**, thereby forming third mixed sample **224***b*.

[0080] The nozzle **202** can then reconfigure again for deposition of the third precursor on the same spot locations (e.g., thereby mixing the precursors in place on the substrate). For example, the valve **204** can switch orientations to couple the third reservoir **210** of supply **212** to nozzle **202**. At stage **232**, nozzle **202** can be re-aligned with the first spot location by moving the nozzle **202** and/or the substrate **214**, and a predetermined seventh amount of third precursor (e.g., corresponding to a desired composition of the ultimate multielement material corresponding to the spot location) can be dispensed from third reservoir **210** to the first spot location via nozzle **202**, thereby forming a first final sample **216***c* (e.g. formed of a combination of a first amount of first precursor, a fourth amount of second precursor, and a seventh amount of third precursor). As shown at stage **234**, the nozzle **202** can then be re-aligned with the second spot location, for example, by moving the nozzle **202** and/or the substrate **214**, and a predetermined eighth amount of third precursor (which eighth amount may be different than the seventh amount of third precursor in sample **216***c*) can be dispensed from third reservoir **210** to the second spot location via nozzle **202**, thereby forming second final sample **218***c*. As shown at stage **236**, the nozzle **202** can then be re-aligned with the third spot location, for example, by moving the nozzle **202** and/or the substrate **214**, and a predetermined ninth amount of third precursor (which ninth amount may be different than the seventh amount of third precursor in sample **216***c* and/or the eighth amount of third precursor in sample **218***c*) can be dispensed from third reservoir **210** to the third spot location via nozzle **202**, thereby forming third final sample **224***c*.

[0081] The reconfiguration of nozzle **202** and deposition of precursor can be repeated any number of times according to the composition defined by the combinatorial approach. After depositing of all sample spots, the substrate **214** can be subjected to thermal shock as described elsewhere herein, so as to form an array of multielement materials of different compositions on the substrate for subsequent screening. Alternatively, in some embodiments, after dispensing of one precursor (e.g., after deposition of first precursor in stage **222**, after deposition of second precursor in stage **230**, and/or after deposition of third precursor in stage **236**) on all desired spots of the substrate **214**, the substrate **214** can be subjected to thermal shock or at least to a thermal treatment prior to beginning dispensing of the next precursor. In some embodiments, such independent treatment of the precursors may help in mixing the elements of the deposited precursor with elements from subsequent precursor depositions. Alternatively or additionally, the system can proceed with deposition of additional precursor depositions on spot locations without an intervening thermal shock.

[0082] In some embodiments, instead of independent deposition of separate precursors on each spot location on the substrate, precursors can be premixed according to desired compositions and then applied directly to a corresponding spot location. For example, FIG. **2**B illustrates an exemplary operation for dispensing of pre-mixed precursors on substrate **214** via nozzle **202**. Similar to FIG. **2**A, a precursor supply **242** having three reservoirs **244**, **246**, **248** can be fluidically coupled to nozzle **202** via a multi-position valve **204**. However, instead of a single precursor in each reservoir, supply **242** maintains a different combination of precursors in each reservoir. For example, first reservoir **244** can have a first ratio of multiple precursors (e.g., three or more) corresponding to a first spot location, second reservoir **246** can have a second ratio of the multiple precursors corresponding to a second spot location, and third reservoir **248** can have a third ratio of the multiple precursors corresponding to a third spot location.

[0083] Although FIG. **2**B illustrates only three reservoirs, supply **242** can include any number of reservoirs, for example, corresponding to the number of different spot locations and/or the number of different combinations to be deposited on the substrate for screening. Indeed, the example of FIG. **2**B illustrates three reservoirs and corresponding deposited spots for simplicity only, but practical embodiments may include more than three reservoirs and more deposited spots (e.g., on the order of 10s, 100s, or even 1000s). Moreover, although the example of FIG. **2**B suggests deposition from one reservoir on a single sample spot, embodiments of the disclosed subject matter are not limited thereto. Rather, mixed precursors from a reservoir can be deposited on multiple spots, for example, to provide the samples with the same compositions for redundant testing and/or to provide different material compositions (e.g., in a manner similar to that described with FIG. **2**A above or FIG. **2**C below).

[0084] At stage **240**, nozzle **202** can be aligned with a first spot location, for example, by moving nozzle **202** with respect to substrate **214**, by moving substrate **214** with respect to the nozzle **202**, or both. A predetermined amount of first premixed precursors (e.g., corresponding to a desired composition of the ultimate multielement material corresponding to the spot location) can be dispensed from first reservoir **244** to the first spot location via nozzle **202**, thereby forming first sample **250**. As shown at stage **254**, the nozzle **202** can then be aligned with a second spot location, for example, by moving the nozzle **202** and/or the substrate **214**, and the valve **204** can switch orientations to couple the second reservoir **246** of supply **242** to nozzle **202**. A predetermined amount of second premixed precursor (which amount may be substantially the same as that of the first premixed precursor forming first sample **250**) can then be dispensed from second reservoir **246** to the second spot location via nozzle **202**, thereby forming second sample **252**.

[0085] As shown at stage **258**, the nozzle **202** can then be aligned with a third spot location, for example, by moving the nozzle **202** and/or the substrate **214**, and the valve **204** can switch orientations to couple the third reservoir **248** of supply **242** to nozzle **202**. A predetermined amount of third premixed precursor (which amount may be substantially the same as that of the first premixed precursor forming first sample **250** and/or the second premixed precursor forming second sample **252**) can then be dispensed from third reservoir **248** to the third spot location via nozzle **202**, thereby forming third sample **256**. After depositing of all sample spots, the substrate **214** can be subjected to thermal shock as described elsewhere herein, so as to form an array of multielement materials of different compositions on the substrate for subsequent screening.

[0086] In some embodiments, instead of premixing precursors, the precursors can be mixed from separate supplies according to desired compositions en route or just prior to dispensing via nozzle (e.g., on-the-fly mixing). For example, FIG. **2**C illustrates an exemplary operation for dispensing of on-the-fly mixed precursors on substrate **214** via nozzle **202**. Similar to FIG. **2**A, precursor supply **272** can have three reservoirs **266**, **268**, **270** with different precursors contained therein. However, instead of a multi-position valve **204**, each reservoir **266**, **268**, **270** can have a respective valve **264***a*, **264***b*, **264***c* that regulates flow therefrom to mixing conduit **262** and/or nozzle **202** to achieve a desired ratio of precursors corresponding to the particular spot location.

[0087] Although FIG. **2**C illustrates only three reservoirs, supply **272** can include any number of reservoirs, for example, corresponding to the number of different precursors required to form the different material combinations according to the combinatorial approach (e.g., three to eight precursors corresponding to three to eight elements in each multielement material). Indeed, the example of FIG. **2**C illustrates three precursors and corresponding deposited spots for simplicity only, but practical embodiments may include more than three precursors and more deposited spots (e.g., on the order of 10s, 100s, or even 1000s). Moreover, although the example of FIG. **2**C suggests inclusion of each precursor in the deposited mixture on each sample spot, embodiments of the disclosed subject matter are not limited thereto. Rather, a precursor can be included in one, some, or all of the deposited mixtures, depending on the details of the designed combinatorial approach.

[0088] At stage **260**, nozzle **202** can be aligned with a first spot location, for example, by moving nozzle **202** with respect to substrate **214**, by moving substrate **214** with respect to the nozzle **202**, or both. Flow from each reservoir **266-270** can be controlled via the respective valves **264***a*-**264***c* to provide a desired first ratio of precursors (e.g., corresponding to a desired composition of the ultimate multielement material corresponding to the first spot location) to mixing conduit **262**. The resulting first mixture of precursors can thus be dispensed to the first spot location via nozzle **202**, thereby forming first sample **274**. As shown at stage **278**, the nozzle **202** can then be aligned with a second spot location, for example, by moving the nozzle **202** and/or the substrate **214**. Flow from each reservoir **266-270** can be controlled via the respective valves **264***a*-**264***c* to provide a desired second ratio of precursors (e.g., corresponding to a desired composition of the ultimate multielement material corresponding to the second spot location) to mixing conduit **262**. The resulting second mixture of precursors can then be dispensed to the second spot location via nozzle **202**, thereby forming second sample **276**. Similarly, as shown at stage **282**, the nozzle **202** can then be aligned with a third spot location, for example, by moving the nozzle **202** and/or the substrate **214**. Flow from each reservoir **266-270** can be controlled via the respective valves **264***a*-**264***c* to provide a desired third ratio of precursors (e.g., corresponding to a desired composition of the ultimate multielement material corresponding to the third spot location) to mixing conduit **262**. The resulting third mixture of precursors can then be dispensed to the third spot location via nozzle **202**, thereby forming third sample **280**. After depositing of all sample spots, the substrate **214** can be subjected to thermal shock as described elsewhere herein, so as to form an array of multielement materials of different compositions on the substrate for subsequent screening.

[0089] Although the description of examples of FIGS. **2**A-**2**C is primarily directed to sequential deposition by a single nozzle, other sequential or parallel deposition techniques are also possible. For example, an array of nozzles can be provided to independently dispense the same or different precursors on different spot locations in parallel. Alternatively or additionally, multiple nozzles can be provided to dispense sequentially or simultaneously dispense precursors on a single spot location. Moreover, although the description of examples of FIGS. **2**A-**2**C suggests that thermal shock is performed after deposition of precursors, one or more intermediate processing steps may be provided after the deposition and prior to the thermal shock. For example, in some embodiments, the deposited precursors can be dried (e.g., via evaporation of the solvent in which the precursors are carried to the spot location) prior to being subjected to the thermal shock.

Exemplary Substrate Configurations

[0090] In some embodiments, a plurality of sample spots with different material compositions can be formed on a substrate according to a combinatorial approach. For example, combinatorial precursor mapping can be employed to provide a large number (e.g., at least 20, at least 50, at least 100, or at least 1000) of different compositions on the substrate for subsequent screening. In some embodiments, the combinatorial precursor mapping can include varying element compositions in a spatial arrangement (e.g., composition of one element varying in a stepwise gradual manner along one linear dimension).

[0091] The substrate can have any shape or configuration, but generally can have a least one exposed substantially-planar surface for deposition of sample spots of precursors thereon. Alternatively, in some embodiments, precursors can be deposited on an intervening material of the substrate (e.g., a metal electrode layer) or a deposition platform (e.g., carbon micro-disk) coupled to the substrate. In some embodiments, the substrate is formed of a material that can withstand exposure to the sintering temperature, for example, carbon, graphite, a refractory material (e.g., refractory metal), etc. Alternatively, in some embodiments where the precursors are sintered using deposition platforms and subsequently coupled to the substrate, the substrate is formed of a material that cannot withstand exposure the sintering temperature, for example, a metal (e.g., copper), a polymer, a composite, etc.

[0092] FIG. **3**A shows an exemplary mapping configuration **300** for a substrate **302**. In the illustrated example of FIG. **3**A, the sample spots **304** (e.g., precursor deposition regions) are arranged in a regular hexagonal array on the substantially-circular substrate **302**. Precursor concentrations (and resulting material compositions after thermal shock) may vary in a gradual and/or predetermined manner across the surface of the substrate **302**. Each sample spot **304**

can have a size (e.g., diameter) of w and a spacing (e.g., minimum separating between adjacent spots) of g. In some embodiments, the sample spot size, spot size spacing, or both can be determined by deposition limitations (e.g., nozzle displacement resolution), synthesis limitations (e.g., to avoid cross-contamination), and/or screening limitations (e.g., to allow separate interrogation by probe head and/or detection by evaluation device). For example, in some embodiments, the sample spot size, w, can be less than or equal to 1 mm, and the spacing, g, can be equal to or greater than the sample spot size, w (e.g., g≥w≤1 mm).

[0093] In some embodiments, the precursors can be deposited directly on a substrate surface, and the multielement materials formed by the precursors after thermal shock can thus be formed directly on and/or integrated with the substrate. For example, FIG. **3**B illustrates a first substrate configuration **310**, where each sample spot **314***a*-**314***d* comprises a separate multielement material **316***a*-**316***d* formed on and in contact with an upper surface of substrate **312**. As discussed elsewhere herein, multielement materials **316***a*-**316***d* can have different material compositions from each other.

[0094] In some embodiments, the precursors can be deposited indirectly on a substrate surface via one or more intermediate layers (e.g., a conductive layer, such as copper, for use in subsequent screening, for example, a common electrode). The multielement materials formed by the precursors after thermal shock can thus be formed on but spaced from a surface of the substrate. For example, FIG. **3**C illustrates a second substrate configuration **320**, where each sample spot **324***a*-**324***d* comprises a separate multielement material **326***a*-**326***d* formed on and in contact with intervening layer **328**, which is in turn formed on and optional in contact with an upper surface of substrate **322**. As discussed elsewhere herein, multielement materials **324***a*-**324***d* can have different material compositions from each other.

[0095] In some embodiments, one or more additional layers can be deposited directly or indirectly on the multielement materials, e.g., for using in subsequent screening, for example, as an individual electrical contact or electrode. For example, FIG. **3**D illustrates a third substrate configuration **330**, where each sample spot **334***a*-**334***d* comprises a separate multielement material **334***a*-**334***d* formed on and in contact with intervening layer **328**, which is in turn formed on and optionally in contact with an upper surface of substrate **332**. Separate cap layers **340***a*-**340***d* can be formed on and in contact with respective upper surfaces of multielement materials **334***a*-**334***d*. For example, cap layers **340***a*-**340***d* can be formed of a metal (e.g., Au) and can act as microdot electrodes. As discussed elsewhere herein, multielement materials **334***a*-**334***d* can have different material compositions from each other.

[0096] In some embodiments, the precursors can be deposited on individual platforms which are subsequently coupled to the substrate, for example, after thermal shock treatment (e.g., when the substrate is formed of a material that may not otherwise survive exposure to the high temperature). For example, FIG. **3**E illustrates a fourth substrate configuration **350**, where each sample spot **354***a*-**354***d* comprises a separate multielement material **356***a*-**356***d* formed on and in contact with respective deposition platforms **358***a*-**358***d*, which are in turn coupled to (e.g., via an adhesive, such as a conductive paste) and optionally in contact with an upper surface of substrate **352** (or an intervening layer formed over the substrate). For example, the deposition platforms **358***a*-**358***d* can be formed of a high-temperature resistant material, such as carbon (e.g., carbon microdisks) or other refractory materials. As discussed elsewhere herein, multielement materials **356***a*-**356***d* can have different material compositions from each other.

[0097] In some embodiments, the plurality of sample spots can be spread over multiple separate substrates, for example, where the size of a single substrate is otherwise insufficient to accommodate all of the sample spots. For example, FIG. **3**F illustrates a fifth substrate configuration **360**, where each sample spot **364***a*-**364***d* comprises a separate multielement material **366***a*-**366***d*. A first subset comprising multielement materials **366***a*-**366***b* can be supported by a first substrate **362***a*, while a second subset comprising multielement materials **366***c*-**366***d* can be supported by a second substrate **362***b*. As discussed elsewhere herein, multielement materials **366***a*-**366***d* can have different material compositions from each other.

[0098] Although FIGS. **3**A-**3**F illustrate a particular number of sample spots, any number of sample spots can be provided on the substrates, for example, corresponding to the number of different material combinations to be screened according to the combinatorial approach. Indeed, the examples of FIGS. **3**B-**3**F illustrate four sample spots for simplicity only, but practical embodiments may include more sample spots (e.g., on the order of 10s, 100s, or even 1000s).

Exemplary Heating Devices

[0099] To convert deposited precursors into a substantially homogeneous solid mixture of multiple elements, the precursors can be subjected a thermal shock treatment comprising one or more high temperature pulses. For example, FIG. **4**A shows an exemplary temperature profile of a thermal shock treatment. A first heating pulse **400** can be applied to a single sample spot (or multiple sample spots on the substrate in parallel). The heating pulse **400** can provide a high temperature TH (e.g., at least 500° C., such as in a range of 1000-3000° C., inclusive) for a relatively short time period t_1 (e.g., less than or equal to 60 second, such as in a range of 0.5 to 30 seconds, inclusive). In some embodiments, the heating pulse **400** can provide a rapid transition to and/or from the high temperature T_H. For example, the heating pulse **400** can exhibit a heating ramp rate RH (e.g., to high temperature T_H from a low temperature TL, such as room temperature (e.g. 20-25° C.) or an elevated ambient temperature (e.g., 100-200° C.)) of at least $10^{2\circ}$ C./s, such as 10^3-$10^{4\circ}$ C./s, inclusive. Alternatively or additionally, the heating pulse **400** can exhibit a cooling ramp rate R_L (e.g., to a low temperature TL from high temperature T_H) of at least $10^{2\circ}$ C./s, such as 10^3-$10^{4\circ}$ C./s, inclusive.

[0100] After a delay t_2, a second heating pulse **402** (which may be substantially identical to the first heating pulse **400**) can be applied to the substrate. In some embodiments, the delay t_2 can of sufficient duration to allow the substrate to be repositioned such that a next sample spot (or set of sample spots) thereon is disposed within the heating zone, for example, to allow conversion of precursors of the next sample spot. In some embodiments, the delay t_2 can be less than a duration of the heating pulse period t_1. Alternatively, the delay t_2 can be substantially equal to or greater than the pulse duration t_1.

[0101] In some embodiments, the heating device can be configured to sequentially heat sample spots on the substrate. For example, FIG. 4B illustrates an exemplary operation for heating of precursors on a substrate **408** via heating device **412** (e.g., a Joule heating element). At stage **410**, a heating zone **414** (e.g., having a temperature substantially matching a high temperature (e.g., sintering temperature) of the thermal shock pulse when the heating device **412** is energized or active) of heating device **412** can be aligned with a first precursor sample **406***a*, for example, by moving heating device **412**, by moving substrate **408**, or both. The heating device **412** can be energized so as to subject the first precursor sample **406***a* to a thermal shock, thereby converting the precursors into a first multielement material **416***a*. The heating device **412** can thus proceed to the next precursor sample. At stage **420**, the heating zone **414** of heating device **412** can be aligned with a second precursor sample **406***b* by moving heating device **412** and/or substrate **408** and then subjecting sample **406***b* to thermal shock to convert it into multielement material **416***b*. Sequential thermal shock treatments can be provided by aligning heating zone **414** with other samples and energizing the heating device **412** in a similar manner in stages **430**, **440** to form additional multielement materials **416***a*-**416***d*. As discussed elsewhere herein, multielement materials **416***a*-**416***d* can have different material compositions from each other.

[0102] Alternatively or additionally, in some embodiments, the heating device can be configured to heat multiple sample spots on the substrate simultaneously. For example, FIG. 4C illustrates an exemplary operation for heating of precursors on a substrate **408** via heating device **452**. At stage **450**, a heating zone **454** (e.g., having a temperature substantially matching a high temperature/sintering temperature of the thermal shock pulse when the heating device **412** is energized or active) of heating device **452** can be aligned with multiple precursor samples **406***a*-**406***d*, for example, by moving heating device **452**, by moving substrate **408**, or both. The heating device **452** can be energized so as to subject the precursor samples **406***a*-**406***d* to a thermal shock, thereby converting the precursors into respective multielement materials **416***a*-**416**, as shown at stage **460** in FIG. 4C. As discussed elsewhere herein, multielement materials **416***a*-**416***d* can have different material compositions from each other.

[0103] Although FIGS. 4B-4C illustrate a particular number of sample spots, any number of sample spots can be provided on the substrates, for example, corresponding to the number of different material combinations to be screened according to the combinatorial approach. Indeed, the examples of FIGS. 4B-4C illustrate four sample spots for simplicity only, but practical embodiments may include more sample spots (e.g., on the order of 10s, 100s, or even 1000s).

Exemplary Evaluation Devices

[0104] FIG. 5A illustrates an exemplary scanning probe cell configuration **500** that can be used as an evaluation device for electrochemical screening of multielement materials **504***a*-**504***b* formed on a metal electrode layer **502** (Cu) on a substrate. The scanning probe cell configuration **500** comprises a microreactor **506** that can be moved into contact with different multielement materials **504***a*-**504***b* on the substrate for testing of each individually. In the illustrated example, the microreactor **506** is disposed over an upper surface of first multielement material **504***a*. Channels **508**, **510** are coupled to the microreactor **506** and are constructed to provide inlet and outlet fluid flows, respectively. An inlet channel **514** is connected to an end of channel **508** remote from microreactor **506** for filling and/or providing fresh electrolyte/solution to the microreactor **506**. A reference electrode **516** can also be coupled to the end of channel **508**, while a counter electrode **512** can be provided to an interior volume of the microreactor **506**, for example, at a location opposite the outlet channel **510**. The sample material **504***a* on metal electrode layer **502** can act as a working electrode, thereby forming a three-electrode setup in the microreactor **506** for rapid electrochemical screening (e.g., by linear scanning sweeps, cycle voltammetry, obtaining electrochemical impedance spectra (EIS), or any other electrocatalytic property characterization). After testing of first material **504***a*, the next material **504***b* can be tested, for example, by moving the scanning probe cell configuration **500**, by moving the substrate, or both.

[0105] FIG. 5B illustrates an exemplary pogo pin testing configuration **520** that can be used as an evaluation device for electrical screening of multielement materials **526***a*-**526***d* formed on a metal electrode layer **524** on substrate **522**. The pogo pin testing configuration **520** comprises a plurality of first pogo pins **530** that contact respective multielement materials **526***a*-**526***d*. Optionally, the pogo pin testing configuration **520** can comprise one or more pogo pins **528** that contact electrode layer **524**, for example, for testing electrical resistance, conductivity, and/or impedance (e.g., which may allow the deconvolution of ionic conductivity contribution from grains and/or grain boundaries) of the fabricated materials **526***a*-**526***d*. In some embodiments, the pogo pin testing configuration **520** can be configured to test the fabricated materials **526***a*-**526***d* in parallel. Alternatively or additionally, the pogo pin testing configuration **520** can include circuitry and/or be controlled by software to test the multielement materials **526***a*-**526***d* sequentially despite the simultaneous contact of pins **530** with the materials **526***a*-**526***d*.

[0106] FIG. 5C illustrates an exemplary optical testing configuration **540** that can be used as an evaluation device for sequential optical screening of multielement materials **544***a*-**544***d* formed on substrate **542**. The optical testing configuration **540** comprises a probe head **546** with an optical source **548** (e.g., laser, laser diode, light-emitting diode (LED), etc.) that emits interrogating light **550** and an optical detector **554** (e.g., photomultiplier tube, photodetector, two-dimensional imaging detector, etc.) for detecting light **552** (e.g., fluorescence) from the first sample **544***a*. After testing of first material **544***a*, the next material **544***b* can be tested, for example, by moving the probe head **546**, by redirecting focal points of the light source **548** and/or collection optics of the detector **554**, by moving the substrate, or any combination of the foregoing.

[0107] FIG. 5D illustrates an exemplary optical testing configuration **560** that can be used as an evaluation device for parallel optical screening of multielement materials **544***a*-**544***d* formed on substrate **542**. Similar to FIG. 5C, the optical testing configuration **560** comprises an optical source **562** that emits interrogating light **564** and an optical detector **570** for detecting light **566**. However, the interrogating light **564** is focused to illuminate multiple samples **544***a*-**544***d* simultaneously, and the detection arm includes collection optics **568** that allows for simultaneous detection of light

566 from multiple samples **544***a*-**544***d*, which may improve throughput of screening multiple samples.

[0108] Although FIGS. **5**A-**5**D illustrate specific examples of an evaluation device, other configurations and/or systems for testing of material properties are also possible according to one or more contemplated embodiments. Moreover, although FIGS. **5**A-**5**D illustrate a particular number of sample spots, any number of sample spots can be provided on the substrates, for example, corresponding to the number of different material combinations to be screened according to the combinatorial approach. Indeed, the example of FIG. **5**A illustrates two sample spots and the examples of FIGS. **5**B-**5**D illustrate four sample spots for simplicity only, but practical embodiments may include more sample spots (e.g., on the order of 10s, 100s, or even 1000s).

Exemplary Multielement Material Synthesis and Screening Methods

[0109] FIG. **6**A illustrates an exemplary method **600** for combinatorial synthesis and screening of multielement materials. The method **600** can initiate at process block **602**, where a substrate can be provided. For example, the provided substrate can be as described above with respect to any of FIGS. **3**A-**3**F. In some embodiments, the provision of process block **602** can include forming one or more intervening layers on the substrate, for example, a metal electrode layer.

[0110] The method **600** can proceed to process block **604**, where sample spots with different intended material compositions can be mapped onto the substrate according to a combinatorial approach. At process block **606**, a first sample spot on the substrate can be selected, and at process block **608**, a first precursor can be deposited on the first sample spot according to the mapped material composition. In some embodiments, the deposition of process block **608** can be performed using a nozzle, for example, in a manner similar to that described above with respect to FIG. **2**A. The method **600** can proceed to decision block **610**, where it is determined if a next sample spot should be selected, for example, to deposit first precursor on a next spot on the substrate. If so, the method **600** can proceed to process block **612**, where the next spot is selected, and the deposition of first precursor in process block **608** is repeated for the selected next spot.

[0111] If no further deposition of the first precursor is desired, the method **600** can proceed from decision block **610** to decision block **614**, where it is determined if the deposited precursor should be subject to pre-sintering. For example, in some embodiments, after dispensing of one precursor on all desired spots of the substrate, the substrate can be subjected to thermal shock or at least to a thermal treatment at process block **616** prior to beginning dispensing of the next precursor. In some embodiments, such independent treatment of the precursors may help in mixing the elements of the deposited precursor with elements from subsequent precursor depositions. Otherwise, if pre-sintering is not desired, the method **600** can proceed from decision block **614** to decision block **616**, where it is determined if additional precursors should be deposited. If so, the method **600** can proceed from decision block **618** to process block **620**, where the next precursor is selected, and the deposition in process block **608** is repeated with the new precursor.

[0112] If no further deposition of any precursors is desired, the method **600** can proceed from decision block **618** to process block **622**, where the deposited precursors are converted to multielement materials by subjecting the substrate to a thermal shock. In some embodiments, the subjecting of process block **622** can be performed using a heating device, for example, in a manner similar to that described above with respect to any of FIGS. **4**A-**4**C. After process block **622**, the method **600** can optionally proceed to process block **624**, where individual electrodes (e.g., Au microdots) can be deposited atop the multielement materials, for example, in a configuration similar to that illustrated in FIG. **3**D.

[0113] The method **600** can proceed to process block **626**, where a first multielement material of the substrate is selected for screening. At process block **628**, the selected multielement material can be testing, for example, with respect to an electrical property, a chemical property, or an optical property. In some embodiments, the testing of process block **628** can be performed using an evaluation device, for example, in a manner similar to that described above with respect to any of FIGS. **5**A-**5**D. In some embodiments, the method **600** can proceed to process block **630**, where the test results can optionally be compared against predetermined criteria, e.g., a minimum or ideal performance value for a particular application. Alternatively, in some embodiments, the comparison can be reserved in favor of simultaneous evaluation of results for multiple fabricated materials, for example, via data mining or machine learning.

[0114] The method **600** can proceed to decision block **632**, where it is determined if a next material should be selected for testing. If so, the method **600** can proceed to process block **634**, where the next material is selected, and the testing in process block **628** is repeated for the selected next material. Alternatively, in some embodiments where the screening is performed in parallel (e.g., in a manner similar to that illustrated in FIGS. **5**B and/or **5**D), the selection of process blocks **626**, **634** and decision block **632** can be omitted.

[0115] If no further testing is desired, the method **600** can proceed from decision block **632** to process block **636**, where a material composition for use in a predetermined application can be determined. In some embodiments, the determination of process block **636** can be selection of one of the tested material samples that exhibit the best performance with respect to one or more predetermined criteria for the particular application, for example, a material that exhibits a highest electrocatalytic activity of those tested. Alternatively or additionally, the determination of process block **636** can act as feedback for a subsequent performance of method **600**, for example, by providing a material composition or range thereof to serve as the basis for a new combinatorial mapping.

[0116] FIG. **6**B illustrates another exemplary method **640** for combinatorial synthesis and screening of multielement materials. The method **640** can initiate at process block **602**, where a substrate can be provided, for example, in a manner similar to that described above with respect to FIG. **6**A. The method **640** can proceed to process block **604**, where sample spots with different intended material compositions can be mapped onto the substrate according to a combinatorial approach, for example, in a manner similar to that described above with respect to FIG. **6**A. The method **640** can then proceed to process block **642**, where precursors can be premixed in separate batches per the mapped material compositions. At process block **606**, a first sample spot on the substrate can be selected, and at process block **644**, a first premixed precursor can be deposited on the first sample spot according to the mapped material composition. In some embodiments, the premixing of process block **642** and/or the deposition of process block **644** can be performed in a manner similar to that described above with respect to FIG. 2B. After process block **642**, performance of blocks **610**, **612**, and **622-636** may otherwise be the same as described above with respect to FIG. **6**A.

[0117] FIG. **6**C illustrates another exemplary method **650** for combinatorial synthesis and screening of multielement materials. The method **650** can initiate at process block **652**, where a substrate can be provided, for example, in a manner similar to that described above with respect to FIG. **6**A. Process block **652** can also include providing separate precursor supplies, for example, in a setup similar to that illustrated in FIG. **2**C. The method **650** can proceed to process block **604**, where sample spots with different intended material compositions can be mapped onto the substrate according to a combinatorial approach, for example, in a manner similar to that described above with respect to FIG. **6**A. At process block **606**, a first sample spot on the substrate can be selected, and at process block **654**, amounts from each precursor supply can be dispensed according to the mapped material composition. In some embodiments, the deposition of process block **654** can be performed in a manner similar to that described above with respect to FIG. **2**C. In some embodiments, the dispensing from the precursor supplies can occur simultaneously, e.g., with mixing from each supply occurring upstream of a nozzle (e.g., en route to deposition). Alternatively, in some embodiments, the dispensing from the precursor supplies can occur sequentially, e.g., with mixing occurring on the substrate and before the nozzle moves to the next spot. After process block **654**, performance of blocks **610**, **612**, and **622-636** may otherwise be the same as described above with respect to FIG. **6**A.

[0118] In FIGS. **6**A-**6**C, although some of blocks **600-654** have been described as being performed once, in some embodiments, multiple repetitions of a particular process block may be employed before proceeding to the next decision block or process block. In addition, although blocks **600-654** have been separately illustrated and described, in some embodiments, process blocks may be combined and performed together (simultaneously or sequentially). Moreover, although FIGS. **6**A-**6**C illustrate a particular order for blocks **600-654**, embodiments of the disclosed subject matter are not limited thereto. Indeed, in certain embodiments, the blocks may occur in a different order than illustrated or simultaneously with other blocks.

Computer Implementation

[0119] FIG. **7** depicts a generalized example of a suitable computing environment **731** in which the described innovations may be implemented, such as aspects of method **600**, method **640**, method **650**, control system **118**, and/or control system **148**. The computing environment **731** is not intended to suggest any limitation as to scope of use or functionality, as the innovations may be implemented in diverse general-purpose or special-purpose computing systems. For example, the computing environment **731** can be any of a variety of computing devices (e.g., desktop computer, laptop computer, server computer, tablet computer, etc.).

[0120] With reference to FIG. **7**, the computing environment **731** includes one or more processing units **735**, **737** and memory **739**, **741**. In FIG. **7**, this basic configuration **751** is included within a dashed line. The processing units **735**, **737** execute computer-executable instructions. A processing unit can be a general-purpose central processing unit (CPU), processor in an application-specific integrated circuit (ASIC) or any other type of processor. In a multi-processing system, multiple processing units execute computer-executable instructions to increase processing power. For example, FIG. **7** shows a central processing unit **735** as well as a graphics processing unit or co-processing unit **737**. The tangible memory **739**, **741** may be volatile memory (e.g., registers, cache, RAM), non-volatile memory (e.g., ROM, EEPROM, flash memory, etc.), or some combination of the two, accessible by the processing unit(s). The memory **739**, **741** stores software **733** implementing one or more innovations described herein, in the form of computer-executable instructions suitable for execution by the processing unit(s).

[0121] A computing system may have additional features. For example, the computing environment **731** includes storage **761**, one or more input devices **771**, one or more output devices **781**, and one or more communication connections **791**. An interconnection mechanism (not shown) such as a bus, controller, or network interconnects the components of the computing environment **731**. Typically, operating system software (not shown) provides an operating environment for other software executing in the computing environment **731**, and coordinates activities of the components of the computing environment **731**.

[0122] The tangible storage **761** may be removable or non-removable, and includes magnetic disks, magnetic tapes or cassettes, CD-ROMs, DVDs, or any other medium which can be used to store information in a non-transitory way, and which can be accessed within the computing environment **731**. The storage **761** can store instructions for the software **733** implementing one or more innovations described herein.

[0123] The input device(s) **771** may be a touch input device such as a keyboard, mouse, pen, or trackball, a voice input device, a scanning device, or another device that provides input to the computing environment **731**. The output device(s) **771** may be a display, printer, speaker, CD-writer, or another device that provides output from computing environment **731**.

[0124] The communication connection(s) **791** enable communication over a communication medium to another computing entity. The communication medium conveys information such as computer-executable instructions, audio or video input or output, or other data in a modulated data signal. A modulated data signal is a signal that has one or more of its characteristics set or changed in such a manner as to encode information in the signal. By way of example, and not limitation, communication media can use an electrical, optical, radio-frequency (RF), or another carrier.

[0125] Any of the disclosed methods can be implemented as computer-executable instructions stored on one or more computer-readable storage media (e.g., one or more optical media discs, volatile memory components (such as DRAM or SRAM), or non-volatile memory components (such as flash memory or hard drives)) and executed on a computer (e.g., any commercially available computer, including smart phones or other mobile devices that include computing hardware). The term computer-readable storage media does not include communication connections, such as signals and carrier waves. Any of the computer-executable instructions for implementing the disclosed techniques as well as any data created and used during implementation of the disclosed embodiments can be stored on one or more computer-readable storage media. The computer-executable instructions can be part of, for example, a dedicated software application or a software application that is accessed or downloaded via a web browser or other software application (such as a remote computing application). Such software can be executed, for example, on a single local computer (e.g., any suitable commercially available computer) or in a network environment (e.g., via the Internet, a wide-area network, a local-area network, a client-server network (such as a cloud computing network), or other such network) using one or more network computers.

[0126] For clarity, only certain selected aspects of the software-based implementations are described. Other details that are well known in the art are omitted. For example, it should be understood that the disclosed technology is not limited to any specific computer language or program. For instance, aspects of the disclosed technology can be implemented by software written in C++, Java, Perl, any other suitable programming language. Likewise, the disclosed technology is not limited to any particular computer or type of hardware. Certain details of suitable computers and hardware are well known and need not be set forth in detail in this disclosure.

[0127] It should also be well understood that any functionality described herein can be performed, at least in part, by one or more hardware logic components, instead of software. For example, and without limitation, illustrative types of hardware logic components that can be used include Field-programmable Gate Arrays (FPGAs), Program-specific Integrated Circuits (ASICs), Program-specific Standard Products (AS SPs), System-on-a-chip systems (SOCs), Complex Programmable Logic Devices (CPLDs), etc.

[0128] Furthermore, any of the software-based embodiments (comprising, for example, computer-executable instructions for causing a computer to perform any of the disclosed methods) can be uploaded, downloaded, or remotely accessed through a suitable communication means. Such suitable communication means include, for example, the Internet, the World Wide Web, an intranet, software applications, cable (including fiber optic cable), magnetic communications, electromagnetic communications (including RF, microwave, and infrared communications), electronic communications, or other such communication means. In any of the above-described examples and embodiments, provision of a request (e.g., data request), indication (e.g., data signal), instruction (e.g., control signal), or any other communication between systems, components, devices, etc. can be by generation and transmission of an appropriate electrical signal by wired or wireless connections.

Fabricated Examples and Experimental Results

[0129] Conventionally, vapor-phase depositions can create a large number of samples using composition gradient. However, vapor-phase deposition requires sophisticated and expensive equipment with a limited choice of materials and substrates. In contrast, the high-throughput synthesis disclosed herein involves two relatively simple steps: (1) combinatorial composition design using metal precursors by formulation in solution phases; and (2) uniform MMNC synthesis by rapid thermal shock of a precursor-loaded carbon support, which drives the rapid precursor decomposition and alloy formation.

[0130] High-throughput synthesis of multimetallic nanoclusters (MMNCs) was achieved by combinatorial composition formulation in the solution phase on a surface-treated carbon support, followed by a rapid thermal-shock treatment. These compositionally-different MMNCs (with similar particle size and structure) were rapidly screened using scanning droplet cell analysis for the electrochemical oxygen reduction reaction (ORR), enabling efficient identification of the two best-performing catalysts. The combination of such high-throughput approaches can establish a facile and reliable pipeline to significantly accelerate discovery of MMNCs as advanced catalytic materials.

[0131] In particular, a series of MMNCs were fabricated, ranging from ternary materials (e.g., PtPdRh) to octonary materials (e.g., PtPdRhRuIrFeCoNi), by adding one element at a time. Precursors for each of the different composition MMNCs were loaded on a carbon nanofiber (CNF) substrate. To form the substrate, electrospun polyacrylonitrile nanofibers were stabilized in air at 533 K (260° C.) for 6 hours, and then carbonized at 1173 K (900° C.) for 2 hours in argon to form untreated CNFs. The CNF films were then further thermally activated at 1023 K (750° C.) for 2 hours in a CO_2 atmosphere in order to create surface defects (e.g., a CO_2-activated CNF (CA-CNF) substrate).

[0132] The individual metal salts or their hydrate forms were dissolved in ethanol at a concentration of 0.05 mol/L. Moreover, 10% (in volume) of 37% HCl was added to $PdCl_2$ solution to complete dissolve $PdCl_2$. The salt precursor solution was loaded onto the suspended CA-CNF film **804** via a print head **802** of a programmable 3D printer **800** (Fisnar F4200N), as shown in FIG. **8**A, or manually using a pipette. The precursor loading was 5 $\mu mol/cm^2$. The precursor salts were used at 1:1 molar ratios between each metallic element in the MMNC design. The printed precursor mixture showed a homogeneous and uniform precursor distribution on the carbon substrates, proved via energy dispersive spectroscopy (EDS) mapping. The initial homogeneity of the formulated precursors can ensure subsequent particle uniformity.

[0133] The precursor-loaded carbon supports were then subjected to high-temperature thermal shock by electrically Joule heating to ~1650 K for a duration of ~500 ms. The samples were electrically connected in series for batch thermal shocking, as shown in FIG. **8**B, or heated individually. In either case, the shock heating induced the rapid decomposition of precursors and the formation of uniformly-dispersed nanoparticles. The surface defects on the carbon support can help to disperse the MMNCs and ensure their size uniformity among the compositionally-different samples, while the rapid thermal-shock treatment can yield single-phase structures due to high-temperature mixing and fast quenching. The thermal shock process was performed with the precursor-loaded CA-CNF film **804** in an argon-filled glovebox. For batch shock processes (thermally-shocking several samples at once), the electrical circuit design involved connecting copper electrodes in series and then thermally shocking all the samples (e.g., glowing regions at **806** in FIG. **8**B) at one time. In order to achieve uniform temperature in these samples in series, the size of the samples was made as close to the same as possible.

[0134] Transmission electron microscopy (TEM) images show the ultra-small and uniform distribution of PtPdRh, PtPdRhRuIr, and PtPdRhRuIrFeCoNi MMNCs, thereby confirming their similar size and dispersity despite the compositional differences. High-resolution high-angle annular dark-field (HAADF) images of the three MMNCs further confirm the similar size distributions, i.e., particles sizes for the PtPdRh, PtPdRhRuIr, and PtPdRhRuIrFeCoNi MMNCs of 3.3 nm±0.8 nm, 3.4 nm±0.7 nm, and 3.7 nm±1 nm, respectively.

[0135] As shown in FIGS. **9**A-**9**B, the sizes and particle dispersion densities of MMNCs synthesized by thermal shock method were compared with examples fabricated by conventional methods, in particular, advanced probe lithography (physical method) or macromolecular template techniques (chemical control). Since particles composed of more than five elements have not been synthesized by the conventional methods, ternary, quaternary, and quinary nanoparticles were selected for comparison. The ternary, quaternary, and quinary MMNCs synthesized by probe lithography exhibit a size distribution of 12.4±1.8 nm, 38.1±3.1 nm, and 30.0±4.7 nm, respectively, with a patterning density of $1/\mu m^2$ (e.g., $1\times10^{-6}/nm^2$) on a flat surface. While much smaller MMNCs (~1.3±0.2 nm) can be synthesized using the macromolecular template method, the dispersion density is quite low (e.g., $1\times10^{-3}/nm^2$) and the composition of choice is also limited. In contrast, in the thermal shock synthesis on defective carbon supports, both the size and dispersal density remain similar for MMNCs with various compositions, which can be useful in comparative studies between MMNCs of different compositions.

[0136] For conventional synthesis methods, incorporating more elements typically results in heterogeneous structures due to the immiscibility among different elements. In contrast, use of the disclosed thermal shock method can overcome immiscibility by creating liquid metal alloy states at high temperature, followed by rapid quenching to largely maintain the alloy mixing. In addition, the multielement materials could help drive the alloy formation by increasing entropy ($\Delta G_{mix}\downarrow=\Delta Hmix-T^*\Delta Smix\uparrow$), which provides kinetic constraints (e.g., severe lattice distortion and sluggish diffusion) such that alloy structures are discouraged from phase separation. The detailed structures of thermal-shock-fabricated MMNCs were fabricated using HAADF and EDS mapping. Low-magnification HAADF and EDS maps confirmed the ultrafine size and high-density dispersion of the nanoclusters, with each element roughly distributed throughout the fiber support without obvious elemental segregation. High-resolution HAADF and EDS images of the ternary, quinary, and octonary samples show particles of ~3-4 nm in size, with each element being uniformly distributed within each nanocluster without clear phase separation or elemental segregation, indicating a solid-solution structure. Note that the final compositions in the MMNCs may be differ slightly from the designed/expected composition, for example, due to differences in metal vapor pressures at high temperatures. The thermal shock method enables alloying at high temperatures while limiting the duration of heating duration, thereby reducing metal losses.

[0137] Macroscopically, powder X-ray diffraction (XRD) profiles illustrate an overall face-centered-cubic (FCC) structure for ternary, quinary, and octonary MMNCs using the Rietveld refinement with a fitted lattice constant of 3.87, 3.82, and 3.76 Å, respectively, as shown in FIG. **10**A. No obvious secondary phases were detected. The decreasing lattice constant can be due to the increasing ratio of non-noble metals (e.g., Fe, Co, Ni) with a smaller size and lattice constant. In addition, synchrotron XRD was performed to detect the fine structure and possible impurity phases in the MMNCs using a much smaller wavelength (λ=0.2113 Å). As shown in FIG. **10**B, all the major peaks can be indexed according to the FCC structure and a fitted lattice constant of 3.87 Å using Rietveld refinement with a reasonably good fit. Namely, the PtPdRh MMNCs still exhibit a largely single FCC phase under synchrotron detection, further confirming the single-phase alloy structure. The diffraction data was converted using q-unit, where $q=(\mathbf{4}\pi\backslash/\lambda)\sin\theta$ so that the data are comparable in the q-unit regardless of the difference in X-ray energy. The solid-solution formation and alloy structural consistency of these MMNCs can be helpful for comparative catalytic studies.

[0138] From a high-throughput perspective, the overall MMNC synthesis protocol involves only printing precursor salts and rapid thermal shock, which are all physical processes that can be easily scaled up. Different metal salt solutions with desired recipes were mixed in the liquid phase. In particular, the combinatorial compositions were designed and formulated in the solution phase using individual precursor solutions with a concentration of 0.05 mol/L. The mixture solutions were then deposited on respective CA-CNF disks (~0.3-inch diameter) with a loading of $100\ \mu L/cm^2$ (i.e., ~5 $\mu mol/cm^2$). These CA-CNF disks were then attached in a pattern (e.g., regular layout) onto a common surface of a copper plate (e.g., copper-foil wrapped silicon wafer) via conductive silver paste. Then, rapid radiative heating (non-direct contact) was used for the MMNC synthesis by positioning a high-temperature heating source above a subset of the samples (e.g., spaced by about ~0.5 cm) and subjected to repeated thermal shock (e.g., heating to 2000 K (1727° C.) for a duration of ~0.5 s, for 3 times). Then the heating element was moved to the next subset of samples until all the samples on the substrate had been heated. A piece of graphitic carbon paper was used as the radiative heating source driven by Joule-heating in an Ar-filled glovebox.

[0139] Using this method, a plate containing a library of 88 samples, including (1) MMNCs in the PtPdRhRuIrFeCoNi compositional space for ORR, and (2) MMNCs in the IrRuAuPdMnFeCoNi space for oxygen evolution reaction (OER), with each composition having 2 samples for cross-validation. The single-phase structure and uniform size distributions of selected MMNCs were also verified. The PtPdRhRuIrFeCoNi compositional space was synthesized and screened using scanning droplet cell electrochemistry, with two promising catalysts quickly identified and further verified in a rotating disk setup. High-throughput electrochemistry was performed to rapidly screen for promising MMNC catalysts. Scanning droplet cell analysis (e.g., as shown in FIG. **5**A) was used as a high-throughput electrochemical screening method for the rapid identification of active electrocatalysts. It integrates an ordinary three-electrode setup into a single tip (e.g., $0.785\ mm^2$ area) for fast, continuous, and potentially automated screening. The copper plate can act as the common current collector from working electrodes during the fast screening. The ORR was used as a model reaction to illustrate one potential implementation of the rapid catalysts screening process, although other screening processes are also contemplated.

ORR is a common cathode reaction to enable fuel cell technologies, yet it is kinetically sluggish with a high overpotential owing to the four-electron transfer process. Discovering high-performance, low-cost, and robust catalysts would therefore be useful to improve ORR and fuel cell operation efficiency.

[0140] The electrochemical tests were performed at room temperature. After moving to a new sample location, the first 30 seconds was used to stabilize the contact between the droplet volume and the selected sample. The electrochemical tests included two 20 mV/s cyclic voltammetry sweeps followed by one 5 mV/s cyclic voltammetry sweep between 1.1 V and 0.45 V versus reversible hydrogen electrode (RHE). A capillary Ag/AgCl electrode reference electrode was flushed with fresh saturated KCl solution every 30 minutes to avoid possible contamination. Because the magnitude of the measured current was around 10^{-4} A, the ohm drop was neglectable. However, the IrRu-based MMNCs samples for OER were found to have apparent corrosion current at high potential, which can obscure the performance and cause uncertainty. Therefore, the following discussion focuses on the PtPd-based compositions for ORR.

[0141] As shown in FIG. **11**A, linear sweep voltammetry (from 1.1 V to 0.45 V) and cyclic voltammetry for different MMNC samples were performed in 0.1 M KOH at a scan rate of 5 mV/s to compare their activity and stability. The blank sample showed very weak activity towards ORR, while the control Pt sample exhibited a good ORR catalytic activity, achieving -3×10^{-4} A at 0.45 V versus RHE. For the MMNC samples, while all share a low onset potential similar to the Pt control, PtPdRhNi and PtPdFeCoNi showed a much larger current at a given potential than others, indicating higher activity. For all MMNC samples, the current continues to increase as the potential decreases without showing a limiting current plateau, due to relatively excessive oxygen being fed to the catalyst such that the reaction was not limited by oxygen mass transfer.

[0142] FIG. **11**B summarizes the specific current at 0.45 V of different samples and reconstructed into a neural network diagram, where the size of the circles represents the magnitude of the sample's specific current at 0.45 V and the lines indicate connections between compositions. Although a relationship between composition and performance is not readily apparent upon initial review of FIG. **11**B, the testing results can be harnessed via data mining and/or machine learning processes to uncover the hidden relationship of elemental compositions to the catalytic performances, which processes can be used to guide subsequent MMNC material design to accelerate catalyst discovery. To gain further insights into the two best-performing catalysts, macroscale and microscale techniques were used for structural characterization. As shown in FIG. **11**C, the synchrotron XRD profiles of these two MMNCs (PtPdRhNi and PtPdFeCoNi) exhibit a single-phase FCC structure under synchrotron detection (λ=0.2113 Å), with a fitted lattice constant of 3.78 and 3.73 Å, respectively, which are very similar to the powder diffraction data. The size distribution of the MMNCs was also verified, as well as their alloy structure by microscopic evaluation. The size remains small and uniformly distributed, while each element is distributed homogeneously throughout the nanoparticles, confirming the alloy structure at nanoparticle level. The synchrotron XRD and TEM data verified the small size and single-phase alloy structure of the MMNCs synthesized using the high-throughput thermal shock method.

[0143] To verify the high performance of the two optimized catalysts (PtPdRhNi and PtPdFeCoNi), electrochemical analysis was performed using a rotating disk electrode (RDE) setup, in particular a Pine Bipotentiostat RDE4 with a glassy carbon (GC) rotating disk electrode (RDE, 0.196 cm^2) and a rotating ring-disk electrode (RRDE, 0.247 cm^2, collection coefficient 0.37). The two MMNCs (PtPdRhNi and PtPdFeCoNi) and the Pt control were synthesized on CA-CNF with a loading of ~10 wt % using the thermal shock synthesis approach. These samples were then prepared into inks for the measurement in 1.0 M KOH at room temperature (22±1° C.). FIG. **12**A showcases the cyclic voltammograms of the PtPdRhNi and PtPdFeCoNi MMNCs and a Pt control sample (10 wt % loading) in an oxygen-saturated electrolyte (1 M KOH). A sharp peak evolved at ~0.85 V for all three samples, which corresponds to the reduction of oxygen. The peak positions of the MMNC catalysts are slightly positive compared with that of Pt as a control, indicating their lower overpotentials and therefore better catalytic activity.

[0144] In addition, both MMNC catalysts exhibit increased peak current densities by about a factor of two as compared to that of Pt. In FIG. **12**B, linear sweep voltammograms of the MMNC catalysts display flat limiting current densities with much higher values and slightly more positive half-wave potentials compared to that of Pt, further confirming the better activity of these MMNCs compared with the Pt control sample. Through the Tafel analysis of FIG. **12**C, slightly smaller Tafel slopes for the MMNCs (32 and 31 mV/dec) were measured as compared with Pt (37 mV/dec), indicating a similar reaction mechanism in ORR. Rotating ring-disk measurement were performed with a small ring-current, and the overall ORR electron number was confirmed to be 3.9~4.0 toward a total oxygen reduction. In addition, the long-term stability of the as-prepared catalysts was tested by chronoamperometry at 0.6 V (versus RHE), as shown in FIG. **12**D. The current density of PtPdRhNi decreased by 36% after 15 hours of operation. Slightly better activity retention (e.g., decreased by 29% after 15 hours of operation) was measured for PtPdFeCoNi. In contrast, the current density of Pt decreased by 39.1% after the same time period, during which most of the activity loss occurred within the first hour. Conclusion

[0145] Any of the features illustrated or described herein, for example, with respect to FIGS. **1**A-**12**D, can be combined with any other feature illustrated or described herein, for example, with respect to FIGS. **1**A-**12**D to provide systems, devices, structures, methods, and embodiments not otherwise illustrated or specifically described herein. For example, any of the substrate configurations of FIGS. **3**A-**3**F can be used in the embodiments of FIGS. **1**A-**2**C and **4**A-**6**C. Other combinations and variations are also possible according to one or more contemplated embodiments. Indeed, all features described herein are independent of one another and, except where structurally impossible, can be used in combination with any other feature described herein.

[0146] In view of the many possible embodiments to which the principles of the disclosed technology may be applied, it should be recognized that the illustrated embodiments are only examples and should not be taken as limiting the scope of the disclosed technology. Rather, the scope is defined by the following claims. We therefore claim all that comes within the scope and spirit of these claims.

1. A method comprising:

(a) depositing one or more first precursors on a first portion of a substrate;

(b) depositing one or more second precursors on a second portion of the substrate, the second portion being spaced from the first portion; and

(c) subjecting each of the first and second portions of the substrate to a first temperature for a first time period so as to convert the deposited one or more first precursors into a first material and to convert the deposited one or more second precursors into a second material,

wherein the first material has a different composition than the second material,

the first temperature is greater than or equal to about 500° C., and

a duration of the first time period is less than about 60 seconds.

2. The method of claim **1**, further comprising:

(d) testing each of the first and second materials with respect to an electrical property, a chemical property, an optical property, or any combination thereof.

3. The method of claim **2**, wherein the testing of (d) comprises measuring an electrochemical impedance spectroscopy (EIS) spectrum for each of the first and second materials, measuring an ionic conductivity for each of the first and second materials, measuring fluorescence of each of the first and second materials, or any combination of the foregoing.

4. The method of claim **2**, further comprising:

(e) determining a composition of a material for use in a predetermined application based at least in part on results of the testing of (d).

5. The method of claim **4**, wherein the determining of (e) comprises selecting one of the first and second materials for use in the predetermined application.

6. The method of claim **4**, wherein the predetermined application comprises use as (i) a catalyst, (ii) a plasmonic nanoparticle, (iii) an energy storage device, (iv) an optoelectronic device, (v) a solid-state electrolyte, (vi) an ion conductive membrane, (vii) a fluorescent material, (viii) a component of any of (i)-(vii), or any combination of (i)-(viii).

7. The method of claim **1**, wherein the first temperature is in a range of 1000° C. to 3000° C., inclusive.

8. The method of claim **1**, wherein a duration of the first time period is in a range of 0.5 seconds to 30 seconds, inclusive.

9. The method of claim **1**, further comprising, prior to (a) and (b):

(g1) depositing one or more third precursors on the first portion of the substrate;

(g2) depositing one or more fourth precursors on the second portion of the substrate; and

(g3) subjecting each of the first and second portions of the substrate to a second temperature for a second time period so to convert the deposited one or more third precursors into a third material and to convert the deposited one or more second precursors into a fourth material,

wherein the depositing of (a) is on the third material and the depositing of (b) is on the fourth material,

the subjecting of (c) converts the one or more first precursors and the third material into the first material and converts the one or more second precursors and the fourth material into the first material.

10. The method of claim **1**, wherein the subjecting of (c) is effective to sinter the one or more first precursors together to form the first material, and to sinter the one or more second precursors together to form the second material.

11. The method of claim **1**, wherein:

the depositing of (a) comprises depositing the one or more first precursors in a vapor phase, in a salt solution, or as a microparticle;

the depositing of (b) comprises depositing the one or more second precursors in a vapor phase, in a salt or oxide solution, or as a microparticle; or

both of the above.

12. The method of claim **1**, wherein the first material is formed as a nanocluster or nanoparticle, the second material is formed as a nanocluster or nanoparticle, or each of the first and second materials is formed as a respective nanocluster or nanoparticle.

13. The method of claim **1**, wherein:

the one or more first precursors comprises at least three elements in a first compositional ratio; and

the one or more second precursors comprise the same elements as the one or more first precursors in a second compositional ration different from the first compositional ratio.

14. The method of claim **1**, wherein the subjecting of (c) comprises:

subjecting the first portion of the substrate to the first temperature for the first time period duration, and then subjecting the second portion of the substrate to the first temperature for the first time period duration; or

simultaneously subjecting the first and second portions of the substrate to the first temperature for the first time period duration.

15. A system comprising:

a dispensing device having a nozzle facing a surface of a substrate and constructed to deposit precursors onto the substrate, at least one of the nozzle and the substrate being movable with respect to the other;

a heating device constructed to generate a first temperature of at least 500° C.; and

a control system operatively coupled to the dispensing device and the heating device, the control system comprising one or more processors and computer readable storage media storing instructions that, when executed by the one or more processors, cause the control system to:

control the dispensing device to position the nozzle with respect to a first portion of the substrate;

deposit, via the nozzle, one or more first precursors on the first portion;

control the dispensing device to position the nozzle with respect to a second portion of the substrate, the second portion being spaced from the first portion;

deposit, via the nozzle, one or more second precursors on the second portion; and

subject, via the heating device, each of the first and second portions of the substrate to the first temperature for a first time period so to convert the deposited one or more first precursors into a first material and to convert the deposited one or more second precursors into a second material,

wherein the first material has a different composition than the second material, and a duration of the first time period is less than 60 seconds.

16. The system of claim **15**, wherein the heating device comprises a Joule heating element, a microwave heating device, a laser, or any combination of the foregoing.

17. The system of claim **15**, wherein the dispensing device comprises an ink jet printer head, an additive manufacturing printer head, a pipette, or any combination of the foregoing.

18. The system of claim **15**, wherein:

the dispensing device comprises at least three reservoirs coupled to the nozzle, each reservoir containing a different element in solution; and

the computer readable storage media stores additional instructions that, when executed by the one or more processors, cause the control system to:

mix, via the dispensing device, the elements in solution from the at least three reservoirs in a first compositional ratio to provide the one or more first precursors for deposition; and

mix, via the dispensing device, the elements in solution from the at least three reservoirs in a second compositional ratio, different from the first compositional ratio, to provide the one or more second precursors for deposition.

19. The system of claim **15**, further comprising:

an evaluation device constructed to measure an electrical property, a chemical property, an optical property, or any combination thereof of a material,

wherein the computer readable storage media stores additional instructions that, when executed by the one or more processors, cause the control system to test, via the evaluation device, each of the first and second materials.

20. The system of claim **19**, wherein the computer readable storage media stores additional instructions that, when executed by the one or more processors, cause the control system to determine a composition of a material for use in a predetermined application based at least in part on results of the testing.

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