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(54) Title: METHODS FOR NON-CONTACT REDUCTION FOR FORMATION OF METAL NANOSTRUCTURES

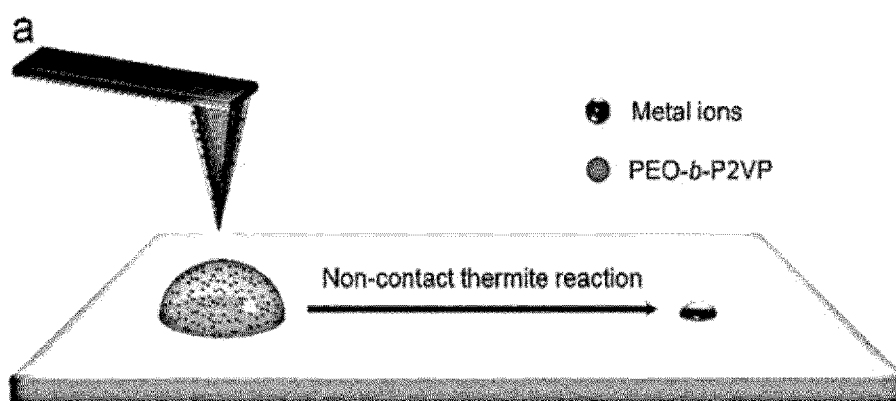


Figure 1A

(57) Abstract: A method of non-contact reduction of metal ions in a nanoreactor containing one or more metal precursors in a block copolymer can include loading a substrate containing the nanoreactors into a furnace at a third zone downstream from first and second zones. In a first zone of the furnace, a reducing material is heated in the presence of a reducing gas flowed into the furnace to react and thereby remove oxidative species from the reducing gas. The reducing gas then flows into the second zone which functions as a cold trap for removing reducing material vapor that may be present with the reducing gas from the first zone. The resulting reducing gas flows into a third zone to generate a reducing environment for the reduction of metal ions in the nanoreactors to thereby form a single nanostructure substantially each of the nanoreactors.

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METHODS FOR NON-CONTACT REDUCTION FOR FORMATION OF METAL
NANOSTRUCTURES

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The benefit of priority to U.S. Provisional Patent Application No. 63/448,191 filed February 24, 2023, is hereby claimed and the disclosure is incorporated by reference in its entirety.

FIELD

[0002] The disclosure relates to methods of forming nanostructure, and, more particularly, to non-contact reducing methods for forming nanostructures from nanoreactors containing metal precursor(s) in a block copolymer.

BACKGROUND

[0003] Materials discovery according to specific requirements is essential to modern industry in many areas, e.g., energy conversion and storage, electronics and semiconductors, catalysis, pharmaceuticals, and advanced manufacturing. Although theoretical calculations have achieved exciting progress and provided insights for this goal, they are not efficient enough when high-throughput screening of complicated systems with various parameters is needed. Artificial intelligence (AI) and machine learning (ML) have the potential to leverage state-of-the-art databases to guide the material design, yet the scarcity of high-quality large datasets with precise control over the synthesis hindered the model training and information extraction.

[0004] Combinatorial synthesis, such as inkjet printing and thin-film deposition, combined with high-throughput screening and analysis techniques, has shown potential for generating large amounts of data. However, it remains a challenge to precisely control the size, composition, and structure of each nanoparticle, which determine the physical, chemical, and catalytical properties. Scanning probe block copolymer lithography (SPBCL), as an emerging combinatorial platform, allows one to print millions of different nanoreactors on a 2×2 cm² chip, and transform each of them into a single nanoparticle, with precise size, composition, structure and position control. But the thermal treatment, either H₂ or Ar annealing, can hardly reduce active metals such as Al, Ti, and Mn, which have shown great potential in manufacturing and catalysis, and make them into single nanoparticles.

SUMMARY

[0005] Methods of the disclosure provide a non-contact thermite reaction that can advantageously increase the number of elemental choices for patterning using a scanning block copolymer lithography (SPBCL) system.

[0006] A method of for forming nanostructures can include providing a substrate comprising nanoreactors disposed on the substrate, each nanoreactor comprising one or more metal precursors and a block copolymer; arranging a reducing material in a first zone of a furnace and the substrate in a third zone of the furnace downstream of the first zone, the first and third zones being separated by a second zone; purifying a reducing gas by flowing the reducing gas into the first zone of the furnace whereby oxidative species present in the reducing gas react with the reducing material, reducing an amount of oxidative species present in the reducing gas to thereby form a reduced oxygen partial pressure reducing gas; flowing the reduced oxygen partial pressure reducing gas through the second zone of the furnace, the second zone whereby reducing material vapor if present in the reduced oxygen partial pressure reducing gas remains trapped in the second zone and a purified reduced oxygen partial pressure reducing gas flows out of the second zone; and reducing the metal precursor in the nanoreactors to a metal or metal alloy by flowing the purified reduced oxygen partial pressure reducing gas into the third zone to generate a reducing atmosphere for decomposition of the metal precursors and formation of metal or metal alloy nanostructures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figure 1A is a schematic illustration of a method in accordance with the disclosure.

[0008] Figure 1B is a schematic illustration of a reduction treatment of a method in accordance with the disclosure.

[0009] Figure 1C is a low-magnitude high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of Al nanoparticle arrays prepared using dip-pen nanolithography (DPN) and a reduction process in accordance with the disclosure. Scale bar is 2 μm .

[0010] Figure 1D is a high-resolution high-angle annular dark field (HAADF) image of a single Al nanoparticle in Figure 1C. Scale bar is 50 nm.

[0011] Figures 1E to 1H are zoomed in HAADF image (1E) of the nanoparticle in Figure 1D with corresponding EDS mapping (1F to 1H). Scale bar in Figure 1E is 20 nm.

[0012] Figure 1I is an HAADF image of an Al nanoparticle formed by a method in accordance with the disclosure. Scale bar 20 nm.

[0013] Figure 1J is an EDS line scan of the dashed line in Figure 1I.

[0014] Figures 2A to 2H are representative HAADF-STEM images of nanoparticles formed of Sc, Ti, V, Cr, Mn, Fe, Ga, and La, respectively, using a method in accordance with the disclosure.

[0015] Figure 3A is a representative HAADF-STEM image of an $\text{Al}_{0.8}\text{Sc}_{0.2}$ nanoparticle for by a method in accordance with the disclosure.

[0016] Figure 3B is a representative HAADF-STEM image of an $\text{Al}_{0.8}\text{Ti}_{0.2}$ nanoparticle formed by a method in accordance with the disclosure.

[0017] Figure 3C is a representative HAADF-STEM image of a $\text{Al}_{0.8}\text{V}_{0.2}$ nanoparticle formed by a method in accordance with the disclosure.

[0018] Figure 3D is a representative HAADF-STEM image of a $\text{Al}_{0.8}\text{Cr}_{0.2}$ nanoparticle formed by a method in accordance with the disclosure.

[0019] Figure 3D is a representative HAADF-STEM image of a $\text{Al}_{0.8}\text{Mn}_{0.2}$ nanoparticle formed by a method in accordance with the disclosure.

[0020] Figures 3F to 3L are representative HAADF-STEM image (Figure 3F) of a $\text{Al}_{0.8}\text{Sc}_{0.04}\text{V}_{0.04}\text{Cr}_{0.04}\text{Mn}_{0.04}\text{La}_{0.04}$ nanoparticle formed by a method in accordance with the disclosure and the corresponding EDS mapping (3G-3L).

[0021] Figures 3M to 3O are representative HAADF-STEM image (3M) of an Al-Ni dimer heterostructure and the corresponding EDS mapping (3N and 3O).

[0022] Figures 3P to 3R are representative HAADF-STEM image (3P) of the Al-Cu dimer heterostructure and the corresponding EDS mapping (3Q and 3R).

[0023] Figure 4A is a low-magnitude HAADF-STEM image of an $\text{Al}_{0.95}\text{Sc}_{0.05}$ nanoparticle array.

[0024] Figures 4B to 4D are representative HAADF-STEM image (4B) of are representative $\text{Al}_{0.95}\text{Sc}_{0.05}$ nanoparticle from Figure 4A, and corresponding EDS mapping (4C and 4D).

[0025] Figures 4E to 4H are HAADF-STEM images of representative $\text{Al}_{0.95}\text{Sc}_{0.05}$ nanoparticles with varied metal contents. The morphology evolved from rod-like structure to circular, and hemispherical structures.

[0026] Figure 4I is a representative HAADF-STEM image of the nanoparticle prepared from $\text{Al}_{0.8}\text{Ga}_{0.2}$ ink.

[0027] Figures 4J and 4K are a representative HAADF-STEM image of the nanoparticle prepared from $\text{Al}_{0.95}\text{Ga}_{0.05}$ ink, and the corresponding EDS linescan of the solid arrow, respectively. The bright dots are Cu nanoparticles due to the Cu contamination on the substrates.

[0028] Figure 5A is an optical image of nanoreactors containing Ir and Mn patterned on a polystyrene-coated glassy carbon substrate.

[0029] Figure 5B is a representative scanning electron microscope (SEM) image of IrMn nanoparticle arrays on glassy carbon after non-contact reduction treatment of the substrate of Figure 5A.

[0030] Figure 5C is an optical image of nanoreactors containing Ru and Mn patterned on a polystyrene-coated glassy carbon substrate.

[0031] Figure 5D is a representative scanning electron microscope (SEM) image of RuMn nanoparticle arrays on the glassy carbon after non-contact reduction treatment of the substrate of Figure 5C.

DETAILED DESCRIPTION

[0032] Methods of the disclosure provide a non-contact reduction method which can allow for reduction of elemental metals and metal alloys that are typically difficult to synthesize using conventional syngas or H₂ annealing. Methods of the disclosure include reduction of nanoreactors containing one or more metal precursors in a block copolymer reactor to a metal or metal alloy nanostructure. The method includes arranging a reducing material in a first zone of a furnace and the substrate having the nanoreactors in a third zone of the furnace downstream of the first zone. The first and third zones are separated by a second zone. A reducing gas is flowed into the furnace and purified by reaction with the reducing material in the first zone. The reducing material interacts with oxidative species present in the reducing gas to thereby remove the oxidative species from the reducing gas. The removal of the oxidative species from the reducing gas improves the reducing ability of the gas and provides a reducing gas having low oxygen partial pressure. This gas is then flowed into the second zone, which is at or about room temperature, and serves as a cold trap, trapping any reducing material vapor present in the reducing gas after the first zone, thereby removing the reducing material vapor and preventing or substantially reducing contamination of the reduction of the metal precursors with a reducing material vapor. The resulting reducing gas then flows into the third zone to create the reducing environment for reduction of the one or more metal precursors in the nanoreactors to metal or metal alloy nanostructures.

[0033] Figures 1A and 1B illustrate a schematic of the method of the disclosure from nanoreactor deposition to the non-contact reducing process performed in the furnace.

[0034] The nanoreactors can be deposited on the substrate using any known methods, including, but not limited to nanolithography methods such as dip pen nanolithography,

polymer pen lithography, and scanning block copolymer lithography. Any suitable substrate can be used that can withstand the heating and reducing environment within the furnace. For example, the substrate can be Si, SiN_x, Ti felt, metal, or glassy carbon.

[0035] The ink deposited to form the nanoreactors includes one or more metal precursors disposed in a block copolymer. The block copolymer can be, for example, poly(ethylene oxide)-b-poly(2-vinyl pyridine) (PEO-b-P2VP). The ink can be an aqueous solution of the block copolymer with the metal precursor(s) dispersed therein. For example, the ink can have a ratio of block copolymer to metal precursor(s) of 64:1 to 2:1 depending on the metal loading desired.

[0036] The furnace can be, for example, a tube furnace divided into three zones. Other types of furnaces that can be sectioned into zones are also contemplated herein. For example, the furnace can be a car bottom furnace, rotary furnace, induction furnace, vacuum furnace, arc furnace, salt bath furnace, bell furnace, pit furnace, pusher furnace, or walking beam furnace.

[0037] The first zone of the furnace is heated to a temperature below the melting temperature of the reducing material. For example, the temperature in the first zone can be about 200 °C below the melting temperature of the reducing material present in the first zone. For example, the temperature of the first zone can be about 450 °C to about 1450 °C, about 500 °C to about 700 °C, about 1000 °C to about 1400 °C, or about 600 °C to about 800 °C. Other suitable temperatures include about 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950, 1000, 1050, 1100, 1150, 1200, 1250, 1300, 1350, 1400, or 1450 °C or any values therebetween or any ranges defined by these values.

[0038] The first zone includes a reducing material. The reducing material can be, for example, one or more of Al, Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Sc, Ti, Mn, lanthanides, and Si. The reducing material can be in any suitable form. For example, the reducing material can be in the form of a foil, a powder, or bulk solid material.

[0039] The second zone is at or about room temperature. The second zone serves as a cold trap for entrapping the reducing material vapor that can be present in the reducing gas after the reaction with the reducing material. This prevents the reducing material vapor from flowing out of the second zone and contaminating the nanostructures to be formed in the third zone. The second zone can be cooled, for example, by exposure to air or other cooling method. The air or other coolant is only in contact with an outer region of the second zone and remains separate from the reducing gas flowing through the second zone.

[0040] The third zone is heated to a temperature of about 150 °C to about 900 °C, about 200 °C to about 800 °C, about 300 °C to about 700 °C, about 500 °C to about 900 °C. Other

suitable temperatures include about 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900 °C or any values therebetween and any ranges defined by these values. For example, the third zone can have a temperature up to 900 °C. Higher temperatures are contemplated herein. For example, higher temperatures can be used with higher temperature resistant substrates. A suitable temperature for reduction can be readily selected by the skilled person based on the metal precursors and substrate used. For example, the third zone can be heated from room temperature to a final temperature of up to 900 °C while flowing the gas through the third zone. The ramping of the temperature in the third zone can include one or more holds at one or more intermediate temperatures and at the final temperature before allowing the reduced nanoreactors to cool. Nanoreactors after the reduction process can be allowed to cool naturally back to room temperature, for example.

[0041] The reducing gas can be H₂ or Ar. After passing through the first zone and reacting with the reducing material, the reducing gas can have a low partial pressure of oxygen. For example, the reducing gas can have a partial pressure of oxygen of 10⁻²⁰ atm to 10⁻⁵⁰ atm (about 10⁻¹⁵ Pa to 10⁻⁴⁵ Pa) after passing through the first zone. . Other suitable partial pressures of oxygen include about 10⁻²⁰, 10⁻²⁵, 10⁻³⁰, 10⁻³⁵, 10⁻⁴⁰, 10⁻⁴⁵, 10⁻⁵⁰ atm and any values therebetween and ranges defined by these values. The gas can be flowed into the furnace at a flow rate of near 0 sccm to 300 sccm. For example, greater than 0 sccm to 300 sccm, 0.1 sccm to about 10 sccm, 100 sccm to 300 sccm, 1 sccm to 250 sccm, or 50 sccm to 150 sccm. Other suitable flow rates include greater than 0, 0.1, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 125, 150, 175, 200, 225, 250, 275, 300 sccm or any values therebetween or ranges defined by these values.

[0042] In embodiments of the method, the method can be performed while drawing a vacuum in the furnace as opposed to flowing the reducing gas through the furnace. The small amount of gas or pressure remaining in the furnace while the vacuum is drawn is treated for oxidative species removal in the first zone with the reducing material and provides the reducing atmosphere in the third zone. In such embodiments, leaking of the vacuum condition and resulting gas from leakage may dominate the flow condition.

[0043] The one or more metal precursors can include one or more metal ions and/or transition metal ions, such as lanthanides. It should be understood that the use of the term “metal precursor” is inclusive of all these types of ions that can be used in the inks as precursors to be reduced. For example, the one or more metal precursors can include ions of elements selected from Al, Ti, Mn, Co, Ni, Au, Cu, Ga, La, Sc, V, Cr, and Fe. Combinations of ions can be included by way of the metal precursors to provide

heterostructure or metal alloy structures upon annealing. For example, the metal precursors can include Al and Ni ions such that an Al-Ni dimer heterostructure is formed after reduction of the nanoreactors. For example, the metal precursors can include Al and Cu ions such that an Al-Cu heterostructure is formed after reduction of the nanoreactors. Other alloys that can be formed by the methods of the disclosure include, but are not limited to, Al in combination with one or more of Sc, Ti, V, Cr, Ni, Cu, and Mn. Based on bulk phase diagrams it was anticipated that Al would tend to form an alloy with Ni and Cu, but methods of the disclosure allowed for formation of a heterostructure as shown in Figures 3M-3R.

[0044] Methods of the disclosure can further include removing the block copolymer. The block copolymer can be etched away, for example, by the reducing environment in the third zone. Other block copolymer removal methods can also be used, such as, for example, H₂ plasma treatment. The resulting nanostructure without the block copolymer can be exposed to air. Upon exposure to air, a protective oxide layer can form, resulting in a metal or metal alloy core being surrounded by a protective oxide shell. Alternatively, the metal nanostructure can be entirely oxidized upon exposure to air. For example, metal nanoparticles formed of Al, Sc, and Fe were observed to form the core-shell structure with a metal core being surrounded by an oxide shell. In contrast, metal nanoparticles formed of Ti, V, Vr, Mn, Ga, and La were observed to fully oxidize upon exposure to air to form metal oxide nanoparticles.

EXAMPLES

[0045] In the following examples, ink solutions were formed by uniformly dispersing metal precursors into a PEO-*b*-P2VP aqueous solution. The ink was then coated onto a dip pen nanolithography tip or a polymer pen tip array for depositing the ink as nanoreactors on a substrate. The reduction process was performed within a tube furnace having three zones. The reducing gas flowed into the tube furnace was H₂. The reducing material present in the first zone was an Al foil. The gas was flowed first through the first zone for reaction with the Al foil to reduce oxidative species within the reducing gas. The gas then flowed into the second zone where metal vapor present in the reducing gas was entrapped and removed from the reducing gas flowing into the third zone. The reducing gas in the third zone generated a reducing atmosphere for reduction of the metal precursors in the nanoreactors to metal, metal heterostructured, or metal alloy nanostructures.

Al Nanoparticle Synthesis

[0046] Aluminum nanoparticles were synthesized using a method in accordance with the disclosure. The ink included PEO-*b*-PEVP and AlCl₃ as the metal precursor. The ink was deposited onto a substrate using dip-pen nanolithography. The substrate was then loaded

into a furnace having three zones. The first zone having the Al foil was heated to a temperature of 660 °C. The oxidative species, such as O₂ and H₂O present in the reducing gas reacted with the Al foil and were removed from the system. The resulting gas having a low oxygen partial pressure P_{O2} was then flowed into the second zone, which was at room temperature. The room temperature second zone functioned as a cold trap for any metal vapor that was present in the reducing gas after passing through the first zone. The second zone of the tube furnace was exposed to air to allow for its cooling to room temperature. The reducing gas then flowed into the third zone to create a reducing environment in which the aluminum ions present in the metal precursor were reduced to form single Al nanoparticles in each nanoreactor. The reducing gas, H₂ gas, was flowed into the tube furnace at 150 sccm flow rate. In the third zone, while the reducing gas was flowed, the nanoreactors were heated to 300 °C at 20 °C/min rate and held at 300°C for 6 hours. The temperature was elevated to 600°C at a ramping rate of 10 °C/min and kept at 600 °C for 6 hours. After the 6 hour hold, the nanoreactors in the third zone were allowed to cool to room temperature naturally, which generally occurred within three hours. Figure 1C is a HAADF-STEM image showing that the Al precursors in the nanoreactors formed single nanoparticles in each nanoreactor. This was also confirmed by HAADF, a representative nanoparticle HAADF image is shown in Figure 1D. Unlike the typical spherical morphology of nanoparticles formed in traditional SPBCL, the Al nanoparticles formed in accordance with the disclosure had smaller contact angles with the substrates and formed a pancake like structure. Referring to Figures 1E-1H, zoomed-in HAADF images and corresponding energy-dispersive X-ray spectroscopy (EDS) mapping showed that a native oxide layer was formed on the surface, providing a core-shell structure in which an Al core was surrounded by an Al₂O₃ shell. Referring to Figure 1I-1J, a linescan across the Al nanoparticle confirmed the core-shell pancake morphology, with a strong Al signal in the central (core) portion.

Nanoparticle Formation with Metals Other than Al

[0047] Methods of the disclosure were also successfully used to form nanoparticles from a variety of other metals. Inks containing a single metal precursor with PEO-*b*-P2VP were prepared as described above. The metal precursor included a metal ion selected from Sc, Ti, V, Cr, Mn, Fe, Ga, or La. The metal precursors used in the inks of the examples included ScCl₃, TiCl₃, VCl₃, CrCl₃·6H₂O, MnCl₂·4H₂O, Fe(OAc)₂, GaCl₃, and LaCl₃. The ink was printed onto a substrate to form nanoreactors using dip-pen nanolithography and the substrate was inserted into a tube furnace for reduction of the metal ions in the precursors. The reducing material present in the first zone was an Al foil and the reducing gas was 150 sccm flow of H₂. The first zone was heated to a temperature of 660 °C and kept at that temperature for the duration of the experiment. The second zone was exposed to air and

kept around room temperature. In the third zone, while the reducing gas was flowed, the nanoreactors were heated to 240 °C from room temperature at a rate of 20 °C/min, and heated to 300 °C at a 0.2 °C/min rate and kept for 6 h. After that, the nanoreactors were heated to 600 °C at a 10 °C/min rate and held at 600 °C for 6 h. Finally, the nanoreactors were cooled down to room temperature naturally (usually within 3 h). Referring to Figure 2A to 2H, the as-formed nanoparticles are shown. Most nanoparticles were fully oxidized after exposure to air, except for Sc and Fe. Similar to Al, Sc and Fe nanoparticles formed a core-shell structure with a metal core surrounded by a metal oxide shell.

Polyelemental Nanostructures

[0048] Metal alloys were also formed using methods in accordance with the disclosure. Due to its light density and high specific strength, Al alloy has been widely used in different areas. It was observed that alloying concentration, as adjusted based on the concentration of precursors included in the ink, affected nanoparticle morphology. Nanosize alloys were synthesized having an 80:20 ratio of Al:other metal. The other metal was Sc, Ti, V, Cr, or Mn.

[0049] The ink used in the methods of the examples was prepared by mixing PEO-*b*-P2VP with the metal precursor(s) in the aqueous solution. The PEO-*b*-P2VP was provided in the ink at a concentration of 5 mg/mL and the polymer to metal ratio was fixed to be 2:1. The metal precursor in the ink was ScCl₃, TiCl₃, VCl₃, CrCl₃·6H₂O, MnCl₂·4H₂O. A 150 sccm H₂ was introduced into the tube furnace. Al foil was used as the reducing material. In the first zone, the Al foil was heated to 660 °C and kept at this temperature during the experiment. The second zone was exposed to air and kept at around room temperature. In the third zone, while the reducing gas was flowed, the nanoreactors were heated to 240 °C from room temperature at a rate of 20 °C/min, and heated to 300 °C at a 0.2 °C/min rate and kept for 6 h. After that, the nanoreactors were heated to 600 °C at a 10 °C/min rate and held at 600 °C for 6 h. Finally, the sample was cooled down to room temperature naturally (usually within 3 h).

[0050] Figures 3A to 3E illustrate the as-formed two-metal alloy nanoparticles. Figures 3F to 3I illustrate that multiple (more than 2) metal alloys could also be generated using the methods of the disclosure. In particular, a metal alloy having the composition Al_{0.8}Sc_{0.04}V_{0.04}Cr_{0.04}Mn_{0.04}La_{0.04} was formed. Referring to Figures 3M-3R, aluminum alloys with Ni and Cu were formed and generated different morphologies from that anticipated by bulk phase diagrams. It was expected that the Al would form alloys with Ni or Cu, but the methods of the disclosure allowed for a dimer heterostructure to be formed.

[0051] Alloy nanoparticles were also formed with 5% other metals, so a ratio of 95:5 Al:other metal. Figure 4A shows the HAADF image of a representative Al nanoparticle array

when a lower (5%) concentration of Sc was included in the ink. A circular morphology was generated as shown in Figures 4B to 4D. It was further observed that reducing ink delivery by adjusting the SPBCL parameters resulted in changes in the morphology to a more rod-like structure (Figures 4E and 4F). Referring to Figures 4G and 4H, the circular structure became multi-circular or hemispherical with increased ink deposition. Referring to Figures 4I to 4K, as compared to the nanoparticles formed with 20% Ga, the nanoparticles formed with 5% Ga has an increased contact angle of Al, resulting in a more dense and thinner oxide layer. It is believed that this oxide layer better protects the metal core. The ink composition with 20% Ga produced an alloy nanoparticle that was more droplet like on the surface.

Mn Alloy Nanoparticles

[0052] Polymer pens consisting of 250,000 pen tips were used to perform SPBCL. Two inks with different metal precursors were sprayed onto the opposite edges of the pen array, resulting in a composition gradient on the pen array surface. In particular, for the ink spraying, a pen array was first blown with N₂ gas to remove any dust particles and treated with air plasma at 30 W for 1 min. A custom-made mask was applied to the pen array to only expose the central 1.5 cm x 1.5 cm area for patterning use. The pen array was secured underneath a spray gun such that the nozzle was 11.5 cm above the pen array and centered over one corner of the exposed area of the pen array. An eco-SPRAY (ViscoTec) spray gun was used to iteratively spray 5 µL of ink at each corner of the array, allowing for drying in between each spray (that is, Mn at two adjacent corners, and Ir or Ru at the other two corners. This gave a metal concentration gradient from the Mn side to the Ir or Ru side. The spray controller was programmed to deliver 5 µL of ink at a rate of 3 mL/min and a pressure of 0.5 bar. After spraying each corner, the entire pen array was placed in an environment of 100% relative humidity for 10 s before allowing it to dry, which improved the spray homogeneity. The spray gun setting was fixed through the whole experiment. The inked pen array and polystyrene-coated substrate were attached to a TERA-print M-series lithography instrument. A lithography experiment was performed in an environment of 90% relative humidity at room temperature such that a 25 x 25 pattern of nanoreactors was deposited with 1 µm spacing. Each droplet was made by moving the substrate into contact with the pen array at an approaching velocity of 50 µm/s with a contact force of 2000-2100 mN, and this force was maintained for 1 s followed by a retraction at a velocity of 100 µm/s of the substrate and continuation of the patterning. The first ink included metal precursors containing Mn ions. The second ink included metal precursors containing Ir or Ru ions. Applying a 25x25 pattern for each pen, about 156,250,00 nanoreactors were successfully made on 2x2 cm² polystyrene coated glassy carbon substrates. Figures 5A and 5C are an optical image of the nanoreactors, showing the pattern of nanoreactors containing Ir and Mn

and the pattern nanoreactors containing Ru and Mn, respectively. The substrate was subjected to a reducing treatment as described above by being loaded into a third zone of a tube furnace. The first zone included an Al foil and was heated to 610°C. The second zone had a temperature at or about room temperature as the second zone was exposed to air. The reducing gas was H₂ introduced under a 150 sccm flow. In the third zone, the nanoreactors were heated with a 1 h ramp from room temperature to 150 °C, then a 6 h ramp from 150 °C to 240 °C, followed by a hold at 240 °C for 12 h, then a ramp to 640 °C in 2 h and a hold at 640 °C for 6 h, followed by cooling to room temperature. The ramp heating in the third zone was performed while the reducing gas was flowed through the third zone. Referring to Figures 5B and 5D, after reduction, single particles were observed to form with decent yield in each nanoreactor.

[0053] The foregoing description is given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, as modifications within the scope of the disclosure may be apparent to those having ordinary skill in the art.

[0054] All patents, patent applications, government publications, government regulations, and literature references cited in this specification are hereby incorporated herein by reference in their entirety. In the case of conflict, the present description, including definitions, will control.

[0055] Throughout the specification, where the compounds, compositions, methods, and/or processes are described as including components, steps, or materials, it is contemplated that the compounds, compositions, methods, and/or processes can also comprise, consist essentially of, or consist of any combination of the recited components or materials, unless described otherwise. Component concentrations can be expressed in terms of weight concentrations, unless specifically indicated otherwise. Combinations of components are contemplated to include homogeneous and/or heterogeneous mixtures, as would be understood by a person of ordinary skill in the art in view of the foregoing disclosure.

What is claimed is:

1. A method of forming nanostructures, comprising:

providing a substrate comprising nanoreactors disposed on the substrate, each nanoreactor comprising one or more metal precursors and a block copolymer;

arranging a reducing material in a first zone of a furnace and the substrate in a third zone of the furnace downstream of the first zone, the first and third zones being separated by a second zone;

purifying a reducing gas by flowing the reducing gas into the first zone of the furnace whereby oxidative species present in the reducing gas react with the reducing material, reducing an amount of oxidative species present in the reducing gas to thereby form a reduced oxygen partial pressure reducing gas;

flowing the reduced oxygen partial pressure reducing gas through the second zone of the furnace, the second zone whereby reducing material vapor if present in the reduced oxygen partial pressure reducing gas remains trapped in the second zone and a purified reduced oxygen partial pressure reducing gas flows out of the second zone; and

reducing the metal precursor in the nanoreactors to a metal or metal alloy by flowing the purified reduced oxygen partial pressure reducing gas into the third zone to generate a reducing atmosphere for decomposition of the metal precursors and formation of metal or metal alloy nanostructures.

2. The method of claim 1 or 2, wherein the first zone has a temperature of about 450 ° to about 1450 °C.

3. The method of any one of the preceding claims, wherein the second zone has a temperature at or about room temperature.

4. The method of any one of the preceding claims, wherein the third zone has a temperature of up to about 900 °C.

5. The method of claim 4, wherein the temperature in the third zone is ramped from room temperature to up to 900 °C while flowing the reducing gas through the third zone.

6. The method of claim 1, wherein the reducing material is one or more of Al, Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Sc, Ti, Mn, lanthanides, and Si. .

7. The method of any one of the preceding claims, wherein the reducing material is present in the form of a foil, a powder, or bulk solid.

8. The method of any one of the preceding claims, wherein the reducing gas is H₂ or Ar.

9. The method of any one of the preceding claims, wherein the reduced oxygen partial pressure reducing gas has a partial pressure of oxygen of P_{O_2} of about 10^{-20} atm to about 10^{-50} atm.

10. The method of any one of the preceding claims, wherein the one or more metal precursors comprise one or more metal ions, lanthanide ions, and transition metal ions.

11. The method of any one of the preceding claims, wherein the one or more metal precursors comprise one or more ions selected from Al, Ti, Mn, Co, Ni, Au, Cu, Ga, La, Sc, V, Cr, and Fe.

12. The method of claim 11, wherein the metal ions comprise Al and Ni or Al and Cu and the metal nanostructures are an Al-Ni or an Al-Cu heterostructure.

13. The method of any one of the preceding claims, comprising forming the pattern of nanoreactors by depositing an ink comprising the block copolymer and the one or more metal precursors using dip pen nanolithography, polymer pen lithography, or scanning block copolymer lithography.

14. The method of any one of the preceding claims, wherein the block copolymer is poly(ethylene oxide)-b-poly(2-vinyl pyridine) (PEO-b-P2VP).

15. The method of any one of the preceding claims, wherein the gas is flowed at a flow rate of greater than about 0 sccm to about 300 sccm.

16. The method of any one of the preceding claims, wherein the nanostructures have an effective average diameter of less than 1 micron.

17. The method of any one of the preceding claims, further comprising exposing the nanostructures to air to thereby form a metal oxide layer surrounding a metal or metal alloy core, or form metal oxide particles.

18. The method of any one of the preceding claims, wherein the substrate is Si, SiNx, Ti felt, metal, or glassy carbon.

19. The method of any one of the preceding claims, wherein substantially each of the nanoreactors contains a single nanostructure after reduction of the metal ions.

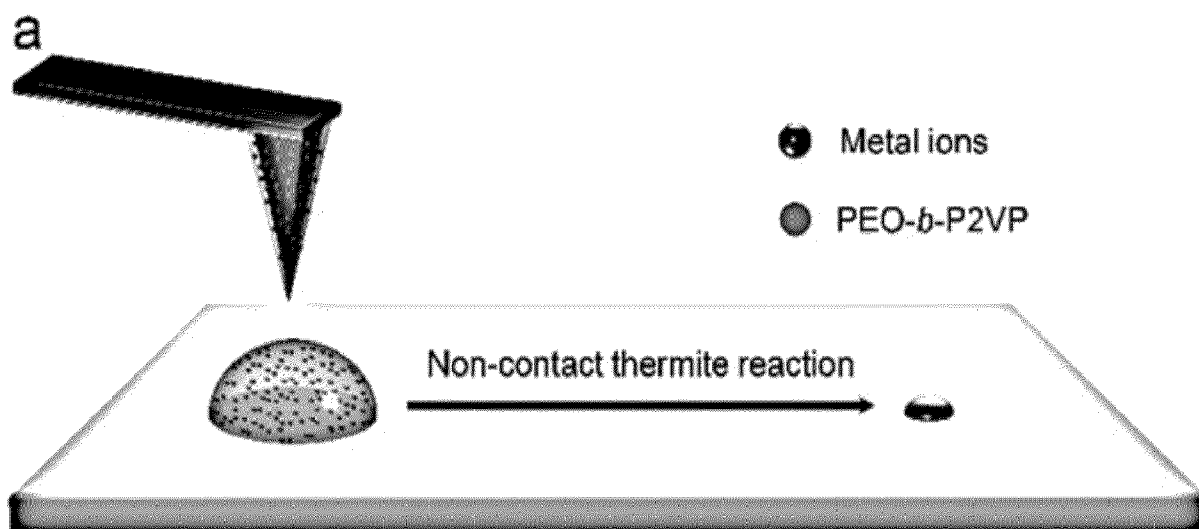


Figure 1A

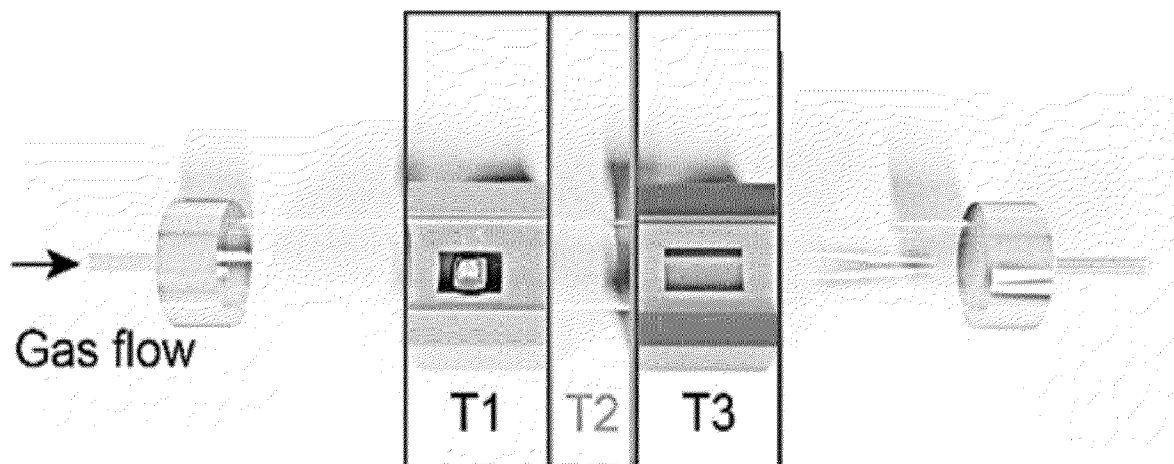


Figure 1B

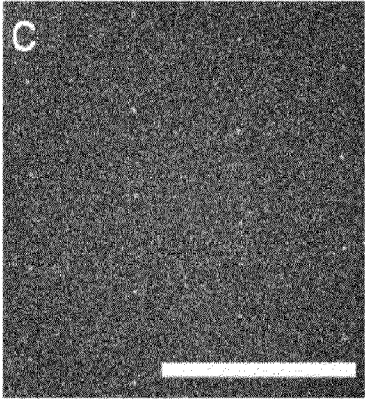


Figure 1C

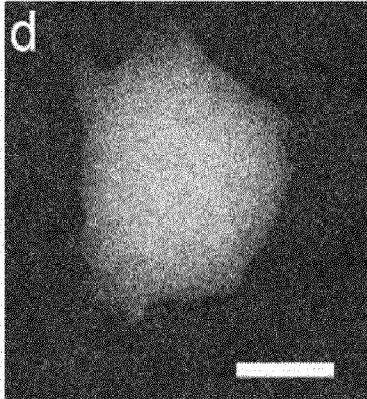


Figure 1D

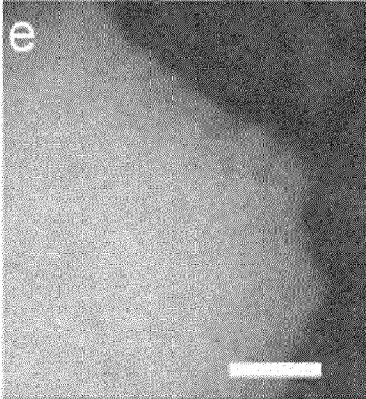


Figure 1E

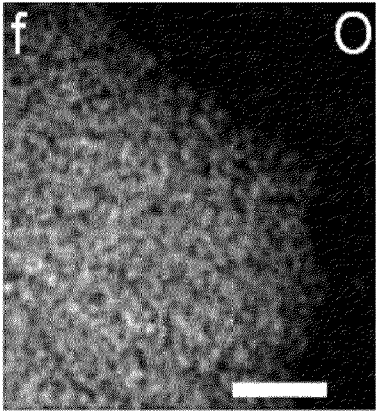


Figure 1F

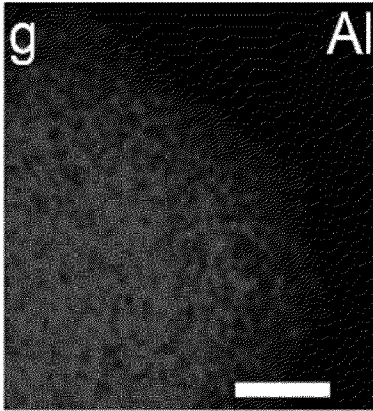


Figure 1G

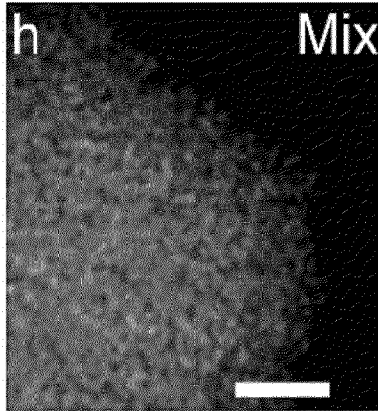


Figure 1H

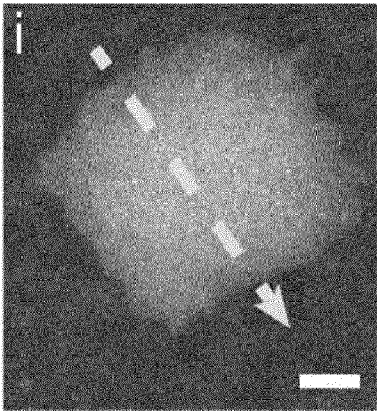


Figure 1I

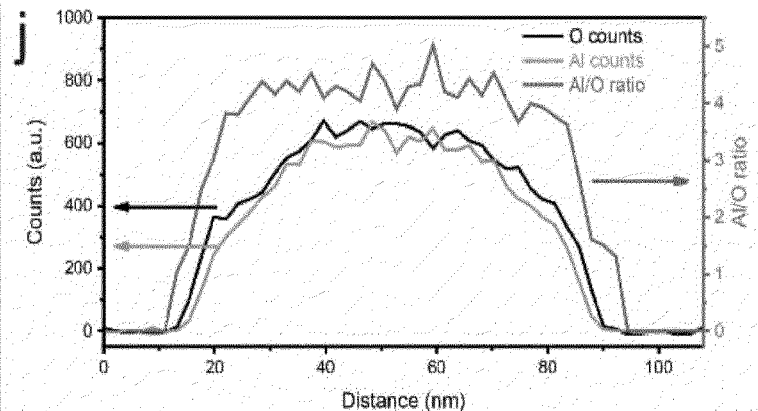


Figure 1J

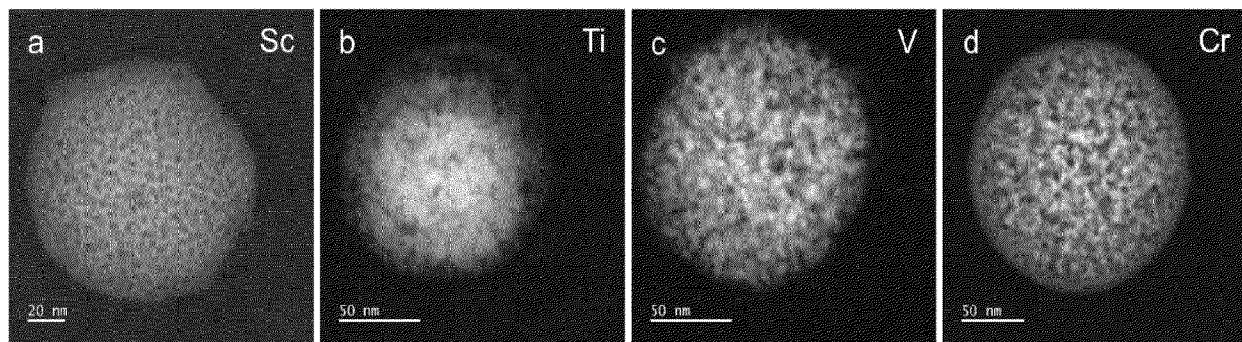


Figure 2A

Figure 2B

Figure 2C

Figure 2D

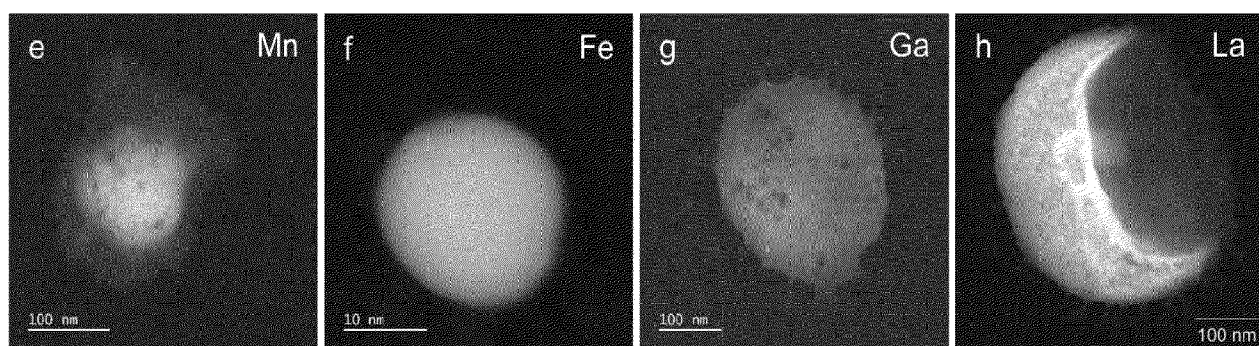


Figure 2E

Figure 2F

Figure 2G

Figure 2H

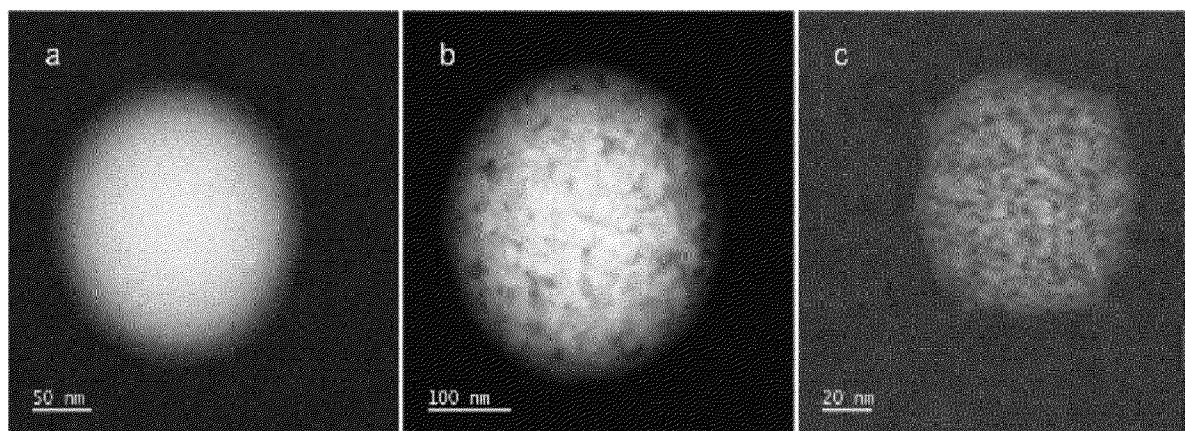


Figure 3A

Figure 3B

Figure 3C

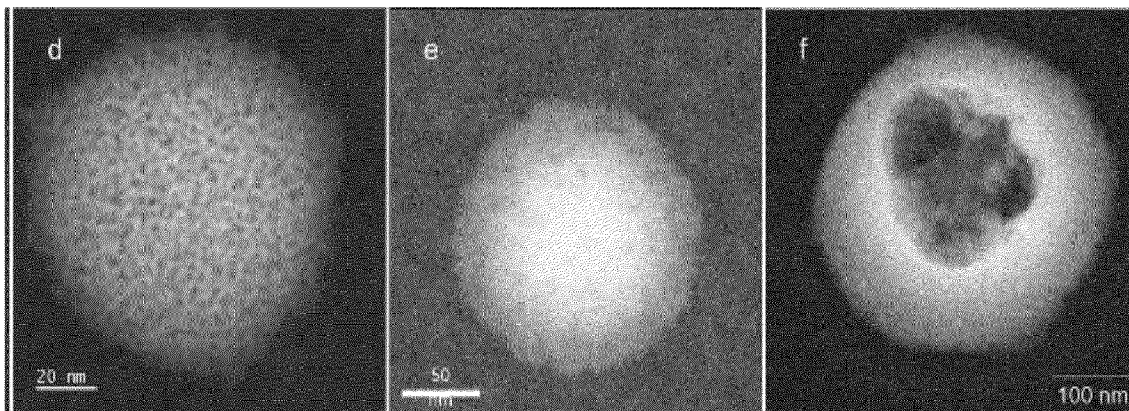


Figure 3D

Figure 3E

Figure 3F

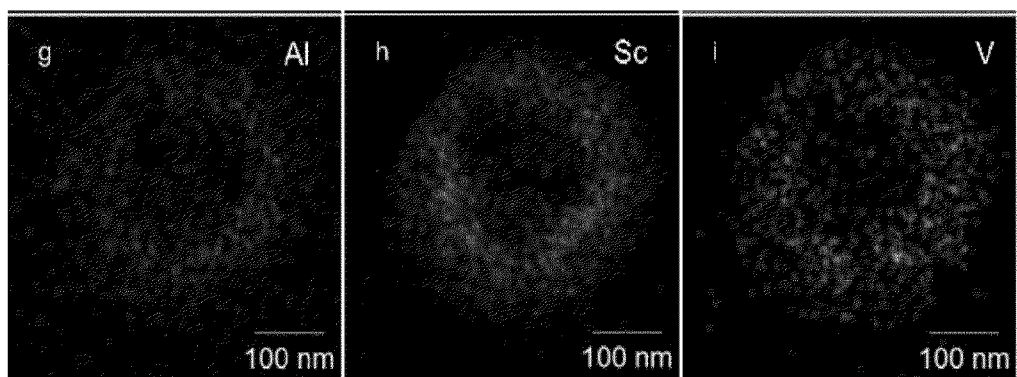


Figure 3G

Figure 3H

Figure 3I

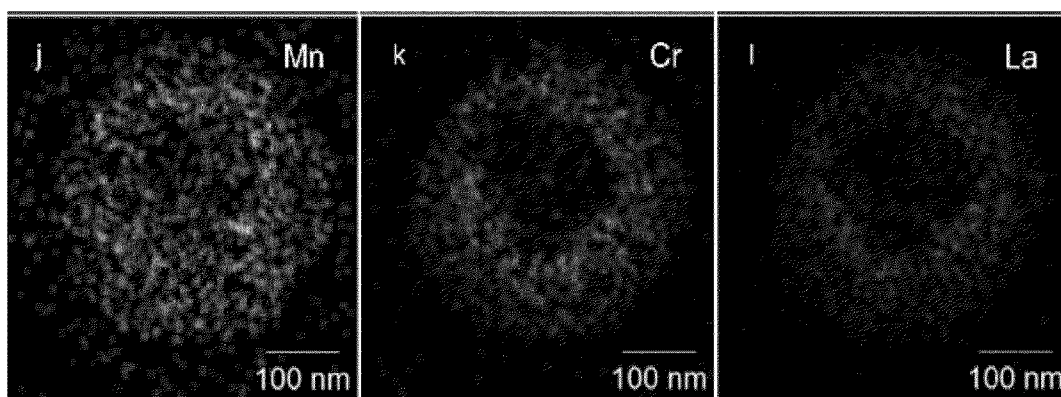


Figure 3J

Figure 3K

Figure 3L

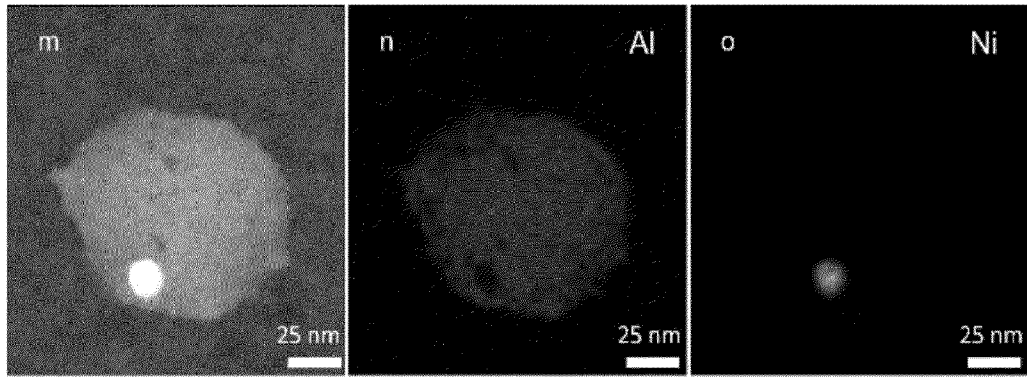


Figure 3M

Figure 3N

Figure 3O

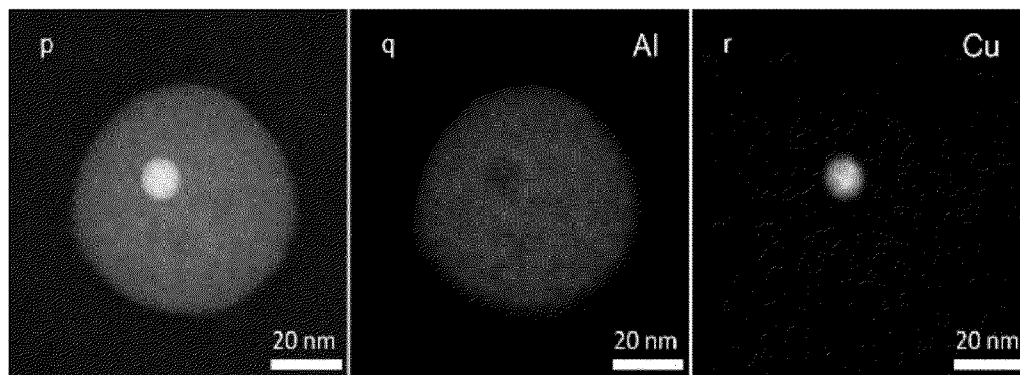


Figure 3P

Figure 3Q

Figure 3R

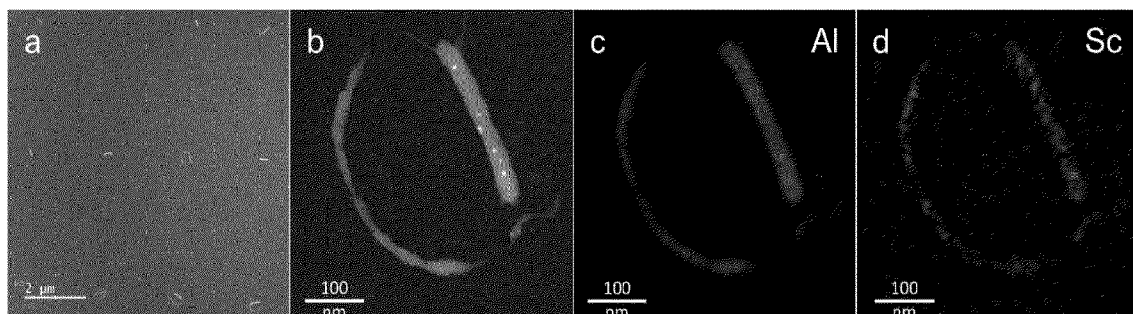


Figure 4A

Figure 4B

Figure 4C

Figure 4D

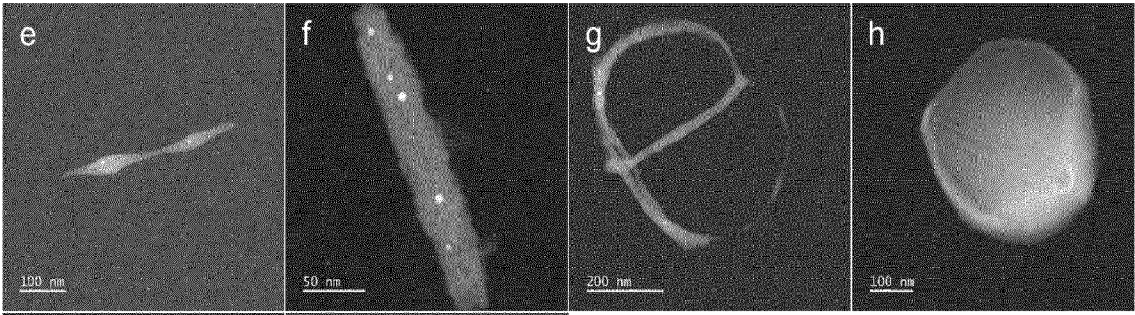


Figure 4E

Figure 4F

Figure 4G

Figure 4H

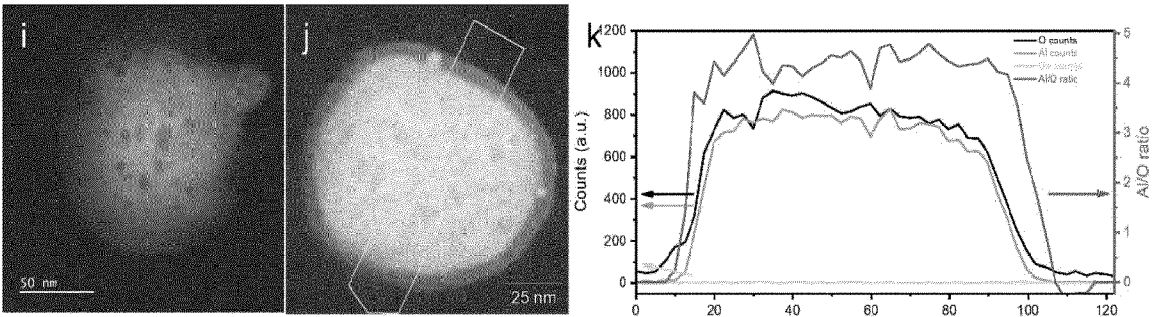


Figure 4I

Figure 4K

Figure 4K

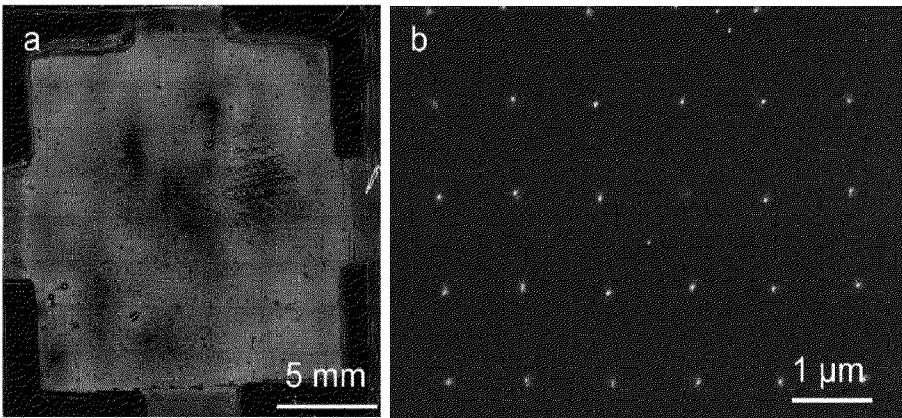


Figure 5A

Figure 5B

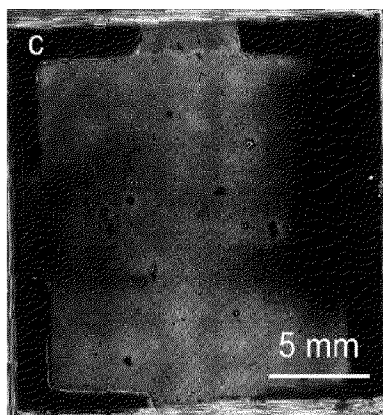


Figure 5C

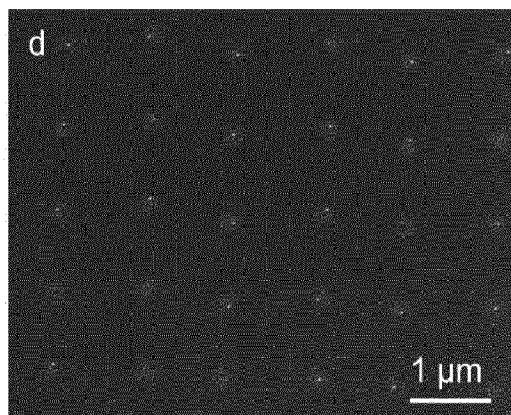


Figure 5D

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 24/17122

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-5, 7-19
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 24/17122

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. B82Y 40/00, G03F 7/00 (2024.01)

ADD. H01B 1/22 (2024.01)

CPC - INV. B82Y 40/00, G03F 7/0002

ADD. H01B 1/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

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

See Search History document

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004/0005258 A1 (Fonash et al.) 8 January 2004 (08.01.2004) Abstract; para [0032], para [0032], para [0038], para [0066], para [0059], para [0030]-[0038]	1-3,6
A	US 2020/0310248 A1 (Northwestern University) 1 October 2020 (01.10.2020) Abstract, para [0005], Fig 1; para [0042]-[0061]	1-3,6
A	US 2021/0163707 A1 (Northwestern University) 3 June 2021 (03.06.2021) Abstract, para [0005], para [0095]-[0105]	1-3,6
A	US 2020/0407812 A1 (Northwestern University) 31 December 2020 (31.12.2020) Abstract, para [0006]-[0009], para [0049]-[0075]	1-3,6
A	US 2021/0008529 A1 (Research Triangle Institute) 14 January 2021 (14.01.2021) Abstract, para [0009], para [00105], Fig 1 para [0052]-[0086]	1-3,6

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

26 April 2024 (26.04.2024)

Date of mailing of the international search report

JUN 26 2024

Name and mailing address of the ISA/US

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