

Multiphasic Crystalline Nanoparticles and Methods of Producing Thereof

Technical Field

The present disclosure refers to a method of producing nanoparticles, in particular a method of producing multiphasic crystalline nanoparticles. The present disclosure also refers to multiphasic crystalline nanoparticles. The present disclosure also refers to a multiphasic crystalline nanoparticle for use in inhibiting bacterial growth.

Background Art

The synthesis of new functional inorganic materials comprising different elements has powered revolutionary technological developments across several epochs and promoted social and economic benefits across various domains. Inorganic compounds/mixtures of metal alloys and ceramics (e.g., oxide and nitride) form the bulk of widely-used materials in modern advanced technologies and broad applications such as catalysis, bioengineering, electronics, clean energy generation and storage, healthcare, urban sustainability and nanomedicine. These inorganic materials may provide access to extraordinary physiochemical properties, e.g., high mechanical strength, ductility and toughness, magnetic and electrochemical properties, that are highly sought after for a broad range of applications such as energy generation and storage, catalysis, and biomaterials. However, conventional metal alloys are typically limited to compositions of one or two principal base metals mixed with other minor components to deter phase segregation. Additionally, developments of facile rapid synthesis routes toward functional multicomponent nanoparticles of metals and ceramics with control of single/mixed crystalline structure configurations as well as understanding their transformative behaviors to enable unexpected properties, however, have remained challenging.

A plethora of top-down physical and/or bottom-up chemical synthesis approaches has been explored to grow nanoparticles (NPs) with defined size, shape, composition, crystallinity and particle structure. For example, transient laser heating is known to anneal a broad range of materials under ambient conditions and to provide spatial and temporal controls of nanostructure patterns and properties. For instance, picosecond pulsed laser ablation of preformed HEA solid targets in liquids generated high entropy alloy nanoparticles (HEA-NPs) with identical compositions; however, the target materials have very strict requirements such as high purity, materials compatibility and thermal stability for high-temperature pre-treatments that inevitably limit materials diversity.

Conventional processes utilising laser irradiation to form nanoparticles often require the prior formation of solid alloy targets, meaning that such processes can only work if pure metals are available. Further, not all metals can mix well to form a single solid target, and the problem is exacerbated when multiple metals in the nanoparticles are desired. Hence, conventional processes are usually limited to simply noble metals or specific combinations of metals already known to mix well in nature.

While multicomponent ceramic NPs were synthesized by nanosecond pulsed laser ablation of precursor-loaded substrates in non-solvent alkanes, the resultant NPs were non-crystalline and phase transitions were not identified. Nanosecond pulsed laser ablation of metal salt precursors in a vacuum had also been described, but the resulting oxide nanomaterials exhibited only a single crystalline phase.

Moreover, at short synthesis durations (<1 s) the influence of process parameters (e.g., rapid heating/cooling rates and brief nucleation and growth durations), are barely understood, further increasing the current challenges to produce the assortments of multicomponent nanoparticles.

Thus, there is a need to find new broad methods of producing multiphasic crystalline nanoparticles that overcome or ameliorate the problems.

Summary

In an aspect of the present disclosure, there is provided a method of producing multiphasic crystalline nanoparticle(s), comprising:

- a. preparing a mixture of at least one metal precursor and solvent;
- b. applying the mixture to a substrate; and
- c. subjecting the mixture to laser irradiation for a duration of about 0.01 ms to about 500 ms, at a power of about 0.1 W to about 100 W to reach peak temperatures of about 250 °C to about 4000 °C,

wherein step (c) comprises laser irradiating a mixture which does not comprise pure metal.

The nanoparticles produced from the presently disclosed method may advantageously contain multiple phases within the same nanoparticle. The presently disclosed method may also be applied to different high-entropy mixture applications, for example high entropy alloys, high entropy ceramics, high entropy oxides, and high entropy nitrides. By changing laser annealing parameters such as power and dwells, the presently disclosed method can produce nanoparticles of various size and composition, advantageously enabling access to nanoparticles with different functional properties. The presently disclosed method may also be easily used in combination with many various substrates, for example porous carbon nanofiber (CNF) and glass substrates. The presently disclosed method may also be performed under nitrogen, air, and may also be performed under ambient conditions, which advantageously makes the reaction easier.

The presently disclosed method also only utilises metal precursors instead of pure metals. Hence, the presently disclosed method can make a variety of nanoparticles without having to first create solid targets comprising the same metals. Additionally, the presently disclosed method does not require a solid target first be made and hence avoids the additional problem of requiring pure metals in order to produce the nanoparticles. Further as not all metals can mix well to form an alloy, the presently disclosed method avoids that same issue by utilizing metal precursors instead of pure metals as starting materials.

The presently disclosed method may be advantageously tuned to accommodate any combination and composition of metal elements. The presently disclosed method may also be used with any metal precursor, including but not limited to chloride, nitrate, and alkoxides. This is advantageous because metal precursors are both more widely available and are easier to handle as compared to the pure metals. Metal precursors are also advantageously more stable as compared to the pure metals. Further, as metals are not required, there is no need to purify said metals, or to mix said metals.

The presently disclosed method also uses laser annealing instead of laser ablation, which is advantageously less energy intensive compared to the latter.

The presently disclosed method may advantageously produce nanoparticles with multiple phases, for example, nanoparticles with biphasic or triphasic crystal phases. In particular, the presently disclosed method may advantageously enable phase transformation of quinary high-entropy metal alloy nanoparticles (HEA-NPs) to either have a single solid-solution face-centered cubic structure or to have multiple face-centered cubic/body-centered cubic structures. Moreover, the presently disclosed method may advantageously enable phase transformation of quinary high-entropy ceramic nanoparticles (HEC-NPs) to either have a tetragonal rutile structure or to have cubic rock salt structure or to have multiple tetragonal rutile/cubic rock salt structures. Such phenomena are usually only observed in bulk metals and bulk ceramics, the presently disclosed method advantageously produces nanoparticles with multiple phases.

In another aspect of the present disclosure, there is provided a multiphasic crystalline nanoparticle comprising at least four metals selected from the group consisting of Li, Be, Na, Mg, K, Ca, Rb, Sr, Ba, Fr, Ra, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Ru, Rh, Pd, Ag, Cd, W, Re, Os, Ir, Pt, Au, Hg, Nb, Ce, Al, Cs, Si, Ge, Sn, Pb and combinations thereof, and at least two phases/and or crystal structures selected

from the group consisting of FCC, BCC, cubic rock salt, tetragonal, rutile tetragonal, hexagonal, orthorhombic, rhombohedral, monoclinic or triclinic crystal systems.

The nanoparticles of the present disclosure may also be advantageously used *in situ* to grow carbonaceous materials such as high-aspect porous graphitic carbon nanostructures and carbon nanotubes for a broad range of application including batteries and capacitors.

The presently disclosed method of synthesising multiphasic crystalline nanoparticles, especially nanoparticles with highly unique surface area and shapes, or different atomic arrangement (phases) and interfaces over multiple length scales (0.1–100 nm), thereby enabling improvements and discovery of new emergent properties and functionalities for surface applications such as sensors and antibacterial/antifouling coatings.

In a further aspect of the present disclosure, there is provided a multiphasic crystalline nanoparticle disclosed herein, for use in inhibiting bacterial growth. In some examples, the multiphasic crystalline nanoparticle disclosed herein may also be used in carbon nanotube growth. In some other examples, the multiphasic crystalline nanoparticle disclosed herein may also be advantageously more efficient in a Hydrogen Evolution Reaction (HER) compared to conventional catalysts. The nanoparticles of the present disclosure may also be advantageously and easily transferred onto other substrates such as poly(ethylene terephthalate) (PET) for further electronics and energy storage applications.

Definitions

Unless otherwise defined herein, scientific and technical terms used in this application shall have the meanings that are commonly understood by those of ordinary skill in the art. Generally, nomenclature used in connection with, and techniques of, chemistry described herein, are those well-known and commonly used in the art.

As used herein, the term “multiphasic” refers to nanoparticles, having more than one phase present in the nanoparticle.

As used herein, the term “crystalline” refers to nanoparticles having crystalline properties. The term also refers to nanoparticles that are not amorphous.

As used herein, the term “ceramic” refers to nanoparticles comprising oxide and/or nitride.

As used herein, the term “substrate” refers to materials where the mixture as disclosed herein may be applied to and used in the laser annealing process. The term “substrate” may be used interchangeably with the term “scaffold”.

As used herein, the term “precursor” refers to salts, compounds and/or oxides of metal elements present before the laser annealing process.

As used herein, the term “atomic size” refers to the distance from the center of the metal atom nucleus to its outermost shell.

As used herein, the term “lattice spacing” refers to the distance between atom centers of adjacent planes in the lattice.

As used herein, the term “lattice cube length”, “lattice parameter”, or “lattice constant” refers to the length between two points on the corners of a unit cell in the metal crystal system and/or phase.

The term “equivolume” as used herein, refers to compositions or mixtures, wherein the individual liquid components of the mixtures are present in the same, substantially the same, or about the same volume.

The term "equimolar" as used herein, refers to compositions or mixtures wherein the individual liquid components of the mixtures are present in the same, substantially the same, or about the same molar concentrations.

Unless the context requires otherwise or specifically stated to the contrary, integers, steps, or elements of the invention recited herein as singular integers, steps or elements clearly encompass both singular and plural forms of the recited integers, steps or elements.

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

As used herein in the specification and in the claims, the phrase "at least," in reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the elements specifically identified within the list of elements to which the phrase "at least one" refers, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, "at least one of A and B" (or, equivalently, "at least one of A or B," or, equivalently "at least one of A and/or B") can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and optionally including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A); in yet another embodiment, to at least one, optionally including more than one, A, and at least one, optionally including more than one, B (and optionally including other elements); etc.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means $\pm 5\%$ of the stated value, more typically $\pm 4\%$ of the stated value, more typically $\pm 3\%$ of the stated value, more typically, $\pm 2\%$ of the stated value, even more typically $\pm 1\%$ of the stated value, and even more typically $\pm 0.5\%$ of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Brief Description of Drawings

The accompanying drawings illustrate disclosed embodiments and serve to explain the principles of the disclosed embodiments. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig. 1

Fig. 1 is a graph showing optical absorption properties of various elements in the visible spectrum.

Fig. 2

Fig. 2 is a scanning electron microscopy (SEM) image of AuPdFeCuNi high entropy alloy nanoparticles (HEA-NPs) generated by laser irradiation at 2 W for 0.25 ms.

Fig. 3

Fig. 3 is a high-resolution transmission electron micrograph (HR-TEM) image of AuPdFeCuNi HEA-NPs generated by laser irradiation at 2 W for 0.25 ms.

Fig. 4

Fig. 4 is a graph showing the wide-angle X-ray scattering (WAXS) data of AuPdFeCuNi HEA-NPs generated by laser irradiation with different laser powers for 0.25 ms.

Fig. 5a

Fig. 5a shows a high-angle annular dark field scanning transmission electron micrograph (HAADF-STEM) image and a series of energy-dispersive spectroscopy (EDS) elemental mapping analysis images of quinary AuPdFeCuNi NPs generated by laser irradiation at 2 W for 0.25 ms.

Fig. 5b

Fig. 5b shows a HAADF-STEM image and EDS image of mono-Pd NPs generated by laser irradiation at 2 W for 0.25 ms.

Fig. 5c

Fig. 5c shows a HAADF-STEM image and a series of EDS elemental mapping analysis images of binary AgCu NPs generated by laser irradiation at 2 W for 0.25 ms.

Fig. 5d

Fig. 5d shows a HAADF-STEM image and a series of EDS elemental mapping analysis images of ternary AuCuFe NPs generated by laser irradiation at 2 W for 0.25 ms.

Fig. 5e

Fig. 5e shows a HAADF-STEM image and a series of EDS elemental mapping analysis images of quaternary AuCuCoFe NPs generated by laser irradiation at 2 W for 0.25 ms.

Fig. 6a

Fig. 6a is a graph showing the EDS atomic fraction line profile of AuPdFeCuNi HEA-NPs after laser annealing at 2 W for 0.25 ms.

Fig. 6b

Fig. 6b is a graph showing the EDS atomic fraction line profile of AuPdFeCuNi HEA-NPs after laser annealing at 2 W for 2.5 ms.

Fig. 6c

Fig. 6c is a graph showing the EDS atomic fraction line profile of AuPdFeCuNi HEA-NPs after laser annealing at 2 W for 25 ms.

Fig. 6d

Fig. 6d is a graph showing the EDS atomic fraction line profile of AuPdFeCuNi HEA-NPs after laser annealing at 2 W for 250 ms.

Fig. 7a

Fig. 7a is a SEM image of AuPdFeCuNi HEA-NPs after laser annealing at 2 W for 2.5 ms.

Fig. 7b

Fig. 7b is a SEM image of AuPdFeCuNi HEA-NPs after laser annealing at 2 W for 25 ms.

Fig. 7c

Fig. 7c is a SEM image of AuPdFeCuNi HEA-NPs after laser annealing at 2 W for 250 ms.

Fig. 8a

Fig. 8a is a SEM image showing the size distributions and area densities of AuPdCuFeNi HEA-NPs after laser annealing at 2 W for 2.5 ms.

Fig. 8b

Fig. 8b is a SEM image showing the size distributions and area densities of AuPdCuFeNi HEA-NPs after laser annealing at 2 W for 25 ms.

Fig. 8c

Fig. 8c is a SEM image showing the size distributions and area densities of AuPdCuFeNi HEA-NPs after laser annealing at 2 W for 250 ms.

Fig. 9a

Fig. 9a shows a HAADF-STEM image and a series of EDS elemental mapping analysis images of AuPdFeCuNi HEA-NPs after laser irradiation at 2 W for 2.5 ms.

Fig. 9b

Fig. 9b shows a HAADF-STEM image and a series of EDS elemental mapping analysis images of AuPdFeCuNi HEA-NPs after laser irradiation at 2 W for 25 ms.

Fig. 9c

Fig. 9c shows a HAADF-STEM image and a series of EDS elemental mapping analysis images of AuPdFeCuNi HEA-NPs after laser irradiation at 2 W for 250 ms.

Fig. 10

Fig. 10 is a graph showing the WAXS data of AuPdFeCuNi HEA-NPs after laser annealing at 2 W for different durations.

Fig. 11

Fig. 11 are images of unlabelled (left) and labelled (right) two-dimensional (2D) selected area electron diffraction (SAED) pattern and a graph showing the 1D integrated intensity plot of the SAED pattern of AuPdFeCuNi HEA-NPs after laser annealing at 2 W for 2.5 ms.

Fig. 12

Fig. 12 are images of unlabelled (left) and labelled (right) second SAED pattern of laser-annealed AuPdFeCuNi HEA-NPs generated by laser irradiation at 2 W for 2.5 ms, with semicircles drawn to indicate *hkl* planes of fcc1, bcc and fcc2 phases.

Fig. 13

Fig. 13 are images of unlabelled (left) and labelled (right) third SAED pattern of laser-annealed AuPdFeCuNi HEA-NPs generated by laser irradiation at 2 W for 2.5 ms, with semicircles drawn to indicate *hkl* planes of fcc1, bcc and fcc2 phases.

Fig. 14a

Fig. 14a is a SEM image of TiNbAlCeV-based high-entropy ceramic nanoparticles (HEC-NPs) on carbon nanofiber (CNF) substrate after laser annealing at 2 W for 0.25 ms.

Fig. 14b

Fig. 14b is a SEM image of TiNbAlCeV-based HEC-NPs on CNF substrate after laser annealing at 6 W for 0.25 ms.

Fig. 14c

Fig. 14c is a SEM image of TiNbAlCeV-based HEC-NPs on CNF substrate after laser annealing at 12 W for 0.25 ms.

Fig. 15

Fig. 15 is a graph showing the integrated WAXS intensity plot TiNbAlCeV-based HEC-NPs after laser annealing at different laser powers for 0.25 ms.

Fig. 16

Fig. 16 shows a series of HAADF-STEM EDS elemental mapping analysis images of TiNbAlCeV-based NPs after laser irradiation at 12 W for 0.25 ms.

Fig. 17a

Fig. 17a is a high-resolution X-ray photoelectron spectroscopy (XPS) spectrum of TiNbAlCeV-based HEC NPs in the Ti *2p* region after laser irradiation at different laser powers for 0.25 ms.

Fig. 17b

Fig. 17b is a high-resolution XPS spectrum of TiNbAlCeV-based HEC NPs in the Nb *3d* region after laser irradiation at different laser powers for 0.25 ms.

Fig. 17c

Fig. 17c is a high-resolution XPS spectrum of TiNbAlCeV-based HEC NPs in the V *2p* region after laser irradiation at different laser powers for 0.25 ms.

Fig. 18a

Fig. 18a is a high-resolution XPS spectrum of TiNbAlCeV-based HEC NPs in the Ce *3d* region after laser irradiation at different laser powers for 0.25 ms.

Fig. 18b

Fig. 18b is a high-resolution XPS spectrum of TiNbAlCeV-based HEC NPs in the Al *2p* region after laser irradiation at different laser powers for 0.25 ms.

Fig. 19a

Fig. 19a is a TEM image of laser-annealed TiON-based NPs after irradiation at 6 W for 2.5 ms dwell.

Fig. 19b

Fig. 19b is a HR-TEM image of laser-annealed TiON-based NPs after irradiation at 6 W for 2.5 ms dwell.

Fig. 19c

Fig. 19c is a series of HAADF-STEM EDS elemental mapping analysis images of TiON-based NPs after irradiation at 6 W for 2.5 ms.

Fig. 20a

Figs. 20a is a graph showing the WAXS spectrum of CrMnFeCoNi (Cantor) NPs after laser irradiation at 2 W for different dwells.

Fig. 20b

Figs. 20b is a graph showing the WAXS spectrum of CrFeCoNiPd (Pd-modified Cantor) NPs after laser irradiation at 2 W for different dwells.

Fig. 21a

Fig. 21a is a graph showing the 2D WAXS profile of AuPdFeCuNi NPs after laser annealing at 6 W for 0.25 ms.

Fig. 21b

Fig. 21b is a graph showing the 1D integrated intensity plots of Fig. 21a.

Fig. 22a

Fig. 22a are the HAADF-STEM and elemental EDS images of AuPdCuFeNi NPs generated on the graphene oxide (GO) layered glass substrate after laser annealing at 2 W for 25 ms.

Fig. 22b

Fig. 22b is the Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) data of the AuPdCuFeNi NPs as produced and shown in Fig. 22a.

Fig. 23a

Fig. 23a is a graph showing the 1D intensity profile plot of the line-focused Gaussian laser beam in the x-axis.

Fig. 23b

Fig. 23b is a graph showing the 1D intensity profile plot of the line-focused Gaussian laser beam in the y-axis.

Fig. 23c

Fig. 23c is a graph showing the correlation of X-ray laser annealing mapping analysis (XLAM) data (black-colored squares) with the principal WAXS peaks of AuPdFeCuNi NPs annealed at laser powers of 3 W, 4 W and 6 W for 0.25 ms.

Fig. 24a

Fig. 24a is a graph showing UV-vis absorption profiles and corresponding adsorption coefficient values of (i) ~60–70 nm thick Pt film, (ii) ~50 μm thick CNF substrate and (iii) ~100–120 nm thick AuPdFeCuNi precursor film on glass.

Fig. 24b

Fig. 24b is a graph showing the plot of simulated peak temperature versus laser power of Pt/carbon sample after a single laser irradiation at various powers for 0.25 ms dwell.

Fig. 24c

Fig. 24c is a graph showing the simulated peak temperature profile of a Pt/carbon sample after laser irradiation at 2 W for 0.25 ms.

Fig. 24d

Fig. 24d is a graph showing the simulated peak temperature profile of a Pt/carbon sample after laser irradiation at 2 W for 2.5 ms.

Fig. 24e

Fig. 24e is a graph showing the simulated peak temperature profile of a Pt/carbon sample after laser irradiation at 2 W for 25 ms.

Fig. 24f

Fig. 24f is a graph showing the simulated peak temperature profile of a Pt/carbon sample after laser irradiation at 2 W for 250 ms.

Fig. 25a

Fig. 25a is a SEM image of mono-Pd NPs on CNF substrate after laser annealing at 10 W for 0.25 ms in ambient air at low magnification.

Fig. 25b

Fig. 25b is a SEM image of mono-Pd NPs on CNF substrate after laser annealing at 10 W for 0.25 ms in ambient air at high magnification.

Fig. 26a

Fig. 26a is a series of photos showing the magnetic properties of AuPdCuFeNi HEA-NPs annealed at 2 W for 0.25 ms.

Fig. 26b

Fig. 26b is a series of photos showing the magnetic properties of AuPdCuFeNi HEA-NPs annealed at 2 W for 25 ms.

Fig. 27a

Fig. 27a is a HR-TEM image of a AuPdFeCuNi NP after laser annealing at 0.6 W for 2.5 ms.

Fig. 27b

Fig. 27b shows a HAADF-STEM image and a series of EDS elemental mapping analysis images of a AuPdFeCuNi NP after laser annealing at 0.6 W for 2.5 ms.

Fig. 27c

Fig. 27c is a graph showing the EDS atomic fraction line profiles of AuPdFeCuNi NPs after laser annealing at 0.6 W for 2.5 ms.

Fig. 28a

Fig. 28a is a schematic demonstrating NPs annealed on a graphene oxide (GO) layer (*) coated on a glass capillary tube (**).

Fig. 28b

Fig. 28b is a SEM image of the AuPdFeCuNi NPs on GO layers in a section of the capillary tube of Fig. 28a, after laser annealing at 2 W for 25 ms. Inset shows an optical image of the same capillary tube after laser annealing.

Fig. 29a

Fig. 29a is a photo showing a tape-assisted removal of laser-induced HEA-NP-coated CNF substrate.

Fig. 29b

Fig. 29b is a photo showing the transfer of NP-coated CNF onto a flexible poly(ethylene terephthalate) (PET) substrate.

Fig. 30a

Fig. 30a is a series of EDS elemental mapping analysis images of AuPdFeCuNi NP grown on carbon nanotubes (CNTs) after irradiation at 10 W for 1 ms.

Fig. 30b

Fig. 30b is a TEM image showing the growth of CNTs catalyzed by AuPdFeCuNi NPs after irradiation at 10 W for 1 ms.

Fig. 30c

Fig. 30c is a HR-TEM image showing the growth of CNTs catalyzed by AuPdFeCuNi NPs after irradiation at 10 W for 1 ms.

Fig. 31a

Fig. 31a is a TEM image showing the growth of CNTs catalyzed by AuPdFeCuNi NPs after irradiation at 10 W for 1 ms.

Fig. 31b

Fig. 31b is a HAADF-STEM micrograph showing the growth of CNTs catalyzed by AuPdFeCuNi NPs - after irradiation at 10 W for 1 ms.

Fig. 31c

Fig. 31c shows a HAADF-STEM and a series of EDS images of a representative AuPdCuFeNi NP in Fig. 31b.

Fig. 32

Fig. 32 is a graph showing the empirical surface diffusivity D_s plots of Au, Cu, Ni, Fe and Pd metals.

Fig. 33

Fig. 33 is a graph showing the polarization curves of four Hydrogen Evolution Reaction (HER) electrodes in 1 M KOH.

Fig. 34

Fig. 34 is a graph showing long-term chronopotentiometry experiments of various electrodes in 1 M KOH after internal resistance correction.

Fig. 35

Fig. 35 is a series of fluorescence images of *E. coli* live cells dyed by SYTO-9 (green) and dead cells dyed by PI (red), after incubation at 37 °C for 24 h.

Fig. 36a

Fig. 36a is a graph showing optical density measurements of *E. coli* growth in the presence of various samples after a 24 h treatment.

Fig. 36b

Fig. 36b is a graph showing optical density measurements of *E. coli* growth in the presence of various samples after a 24 h treatment.

Fig. 37

Fig. 37 is a series of SEM images of mono-Pd NPs generated on CNF substrate after laser annealing at different laser powers and dwells.

Fig. 38a

Fig. 38a is a graph showing the line plots of mean diameters of mono-Pd NPs generated and shown in Fig. 37.

Fig. 38b

Fig. 38b is a TEM image of Pd nanoparticles anchored on the CNF surface after laser irradiation of 2 W for 0.25 ms.

Fig. 39a

Fig. 39a is a graph showing the calculated melting points of Pd versus particle diameter.

Fig. 39b

Fig. 39b is a graph showing the characteristic time analyses of Pd nanoparticle growth at 952 K.

Fig. 40

Fig. 40 is a series of SEM images of mono-Pd NPs generated on CNF substrate after laser annealing at different laser powers and dwells.

Fig. 41

Fig. 41 is a graph showing the Raman spectra of neat CNF substrate after laser irradiation at 6 W for different dwells.

Fig. 42a

Fig. 42a is a SEM image of neat CNF substrate at low magnification.

Fig. 42b

Fig. 42b is a SEM image of neat CNF substrate at high magnification.

Fig. 42c

Fig. 42c is a SEM images of CNF substrate, coated with PdCl₂, at low magnification.

Fig. 42d

Fig. 42d is a SEM image of CNF substrate, coated with PdCl₂, at high magnification.

Fig. 42e

Fig. 42e is a graph showing the diameter measurements of individual uncoated and PdCl₂-coated CNFs. The Pd precursor coating thickness was ~40 nm.

Detailed Disclosure of Embodiments

Rapid and scalable approaches towards multicomponent metal solid solution nanostructures are highly desirable to access new unique property profiles absent in conventional alloys. However, to the best of our knowledge, laser-induced generation of single- and multicomponent metal alloy nanoparticles for millisecond timescales has not been explored and their associated process–structure–property correlations remain elusive.

Herein is described a method of producing a multiphasic crystalline nanoparticle, comprising: (a) preparing a mixture of at least one metal precursor and solvent; (b) applying the mixture to a substrate; and (c) subjecting the mixture to laser irradiation for a duration of about 0.01 ms to about 500 ms and at a power of about 0.1 W to about 100 W to reach a peak temperature of about 250 °C to about 4000 °C, wherein step (c) comprises laser irradiating a mixture which does not comprise pure metal.

Described herein is a laser heating strategy to generate multiphasic crystalline nanoparticles. In particular, described herein is a transient, spatially and temporally controllable laser heating method at millisecond timescales to generate functional high entropy alloy, oxide and nitride nanoparticles on various substrate, for example, conducting carbon substrate and insulating glass substrates.

Further described herein is a method of laser irradiating the same metal salt mixture, but at different millisecond heating times, to provide direct control of the cooling rates thereby producing high entropy alloy multiphasic crystalline nanoparticles with tunable single and multiphasic solid solution characteristics, atomic compositions, nanoparticle morphologies and physicochemical properties.

The method disclosed herein, is capable of being applied to nitride-forming precursors, to enable laser-induced carbothermal reduction and nitridation of high entropy tetragonal rutile oxide multiphasic crystalline nanoparticles to the cubic rock salt nitride phase.

Further described herein are high entropy alloy nanoparticles comprising constituent elements of Au, Pd, Ag, Fe, Ni, Cu and Co. The high energy alloy nanoparticles of the present invention, comprising

multiple components are suitable for a range of nanomaterial applications such as growth of carbon nanotubes, water splitting and antimicrobial applications.

Reducing metal and ceramic compounds to their nanoscale forms, while increasing the number of principal elements with substantial concentrations, enhance the overall diversity in terms of atomic interfaces, phase characteristics, compositions, as well as enable new emergent collective properties and performance, e.g., high mechanical strength, ductility and toughness, electrical, magnetic and electrochemical activities.

These concentrated alloy nanoparticles can provide access to extraordinary physiochemical properties, e.g., high mechanical strength, ductility and toughness, magnetic and electrochemical properties, that are highly sought after for a broad range of applications such as energy generation and storage, catalysis, and biomaterials.

The method as described can be adjusted, by e.g., varying laser power and annealing dwell, to control the various properties of the multiphase crystalline nanoparticles, e.g., nanoparticle shape, morphology, size and size distribution as well as composition.

Further disclosed is a method of studying the structural evolution of high entropy metal alloy nanoparticles and establishing the processing–structure–composition–property correlations by millisecond laser heating with spatially resolved X-ray diffraction. The combination of laser heating with spatially resolved X-ray diffraction facilitates combinatorial studies of phase transitions and reaction pathways of multicomponent nanoparticles. These findings provide a general strategy to design nonequilibrium multicomponent metal alloys and ceramic materials amalgamations for fundamental studies and practical applications such as carbon nanotube growth, water splitting and antimicrobial applications.

In the present invention, there is disclosed a method of producing multiphase crystalline nanoparticle(s), comprising:

- a. preparing a mixture of at least one metal precursor and solvent;
- b. applying the mixture to a substrate; and
- c. subjecting the mixture to laser irradiation for a duration of about 0.01 ms to about 500 ms, at a power of about 0.1 W to about 100 W to reach peak temperatures of about 250 °C to about 4000 °C,

wherein step (c) comprises laser irradiating a mixture which does not comprise pure metal.

The presently disclosed method utilises laser-induced melt-mediated crystallization instead of laser ablation. Laser ablation is typically a high-energy process, with high laser powers of up to 2000 W, and having dwell times of less than 1 μ s. With such high energies and short durations, the precursors are typically transformed into a mixture of volatile components comprising ions, clusters and vapours. Upon cooling, the volatile components nucleate into clusters and aggregate further into particles of larger sizes. Also, at such high energies, the nanoparticles formed only exhibit a single phase, or are amorphous at worse.

In comparison, laser-induced melt-mediated crystallization is a far gentler process that first melts the precursor and allows local diffusion of the atoms within the liquid droplet, followed by solidification into crystalline nanoparticles. Hence, the method of the present invention advantageously produces nanoparticles that are crystalline with multiple phases.

In some embodiments, step (c) comprises subjecting the mixture to laser irradiation for a duration of in a range of at least about 0.01 ms, at least about 0.025 ms, at least about 0.05 ms, at least about 0.075 ms, at least about 0.1 ms, at least about 0.25 ms, at least about 0.5 ms, at least about 0.75 ms, at least about 1 ms, at least about 2.5 ms, at least about 5 ms, at least about 7.5 ms, at least about 10 ms, at least about 20 ms, at least about 25 ms, at least about 50 ms, at least about 100 ms, at least about 200 ms, at least about 250 ms, at least about 300 ms, at least about 400 ms, at least about 500 ms; or from about 0.01 ms to about 500 ms, from about 0.01 ms to about 400 ms, from about 0.01 ms to about 300 ms, from about 0.01 ms to about 250 ms, from about 0.01 ms to about 200 ms, from about 0.01 ms to about 100 ms, from about 0.01

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In some other embodiments, step (c) comprises subjecting the mixture to laser irradiation at a power range in a range of at least about 0.1 W, at least about 0.25 W, at least about 0.5 W, at least about 0.6 W, at least about 0.75 W, at least about 1 W, at least about 2 W, at least about 3 W, at least about 4 W, at least about 5 W, at least about 6 W, at least about 8 W, at least about 10 W, at least about 12 W, at least about 14 W, at least about 16 W, at least about 18 W, at least about 20 W, at least about 40 W, at least about 60 W, at least about 80 W, at least about 100 W; or from about 0.1 W to about 100 W, from about 0.1 W to about 80 W, from about 0.1 W to about 60 W, from about 0.1 W to about 40 W, from about 0.1 W to about 20 W, from about 0.1 W to about 18 W, from about 0.1 W to about 16 W, from about 0.1 W to about 14 W, from about 0.1 W to about 12 W, from about 0.1 W to about 10 W, from about 0.1 W to about 8 W, from about 0.1 W to about 6 W, from about 0.1 W to about 5 W, from about 0.1 W to about 4 W, from about 0.1 W to about 3 W, from about 0.1 W to about 2 W, from about 0.1 W to about 1 W, from about 0.1 W to about 0.75 W, from about 0.1 W to about 0.6 W, from about 0.1 W to about 0.5 W, from about 0.1 W to about 0.25 W, from about 0.25 W to about 100 W, from about 0.25 W to about 80 W, from about 0.25 W to about 60 W, from about 0.25 W to about 40 W, from about 0.25 W to about 20 W, from about 0.25 W to about 18 W, from about 0.25 W to about 16 W, from about 0.25 W to about 14 W, from about 0.25 W to about 12 W, from about 0.25 W to about 10 W, from about 0.25 W to about 8 W, from about 0.25 W to about 6 W, from about 0.25 W to about 5 W, from about 0.25 W to about 4 W, from about 0.25 W to about 3 W, from about 0.25 W to about 2 W, from about 0.25 W to about 1 W, from about 0.25 W to about 0.75 W, from about 0.25 W to about 0.6 W, from about 0.25 W to about 0.5 W, from about 0.5 W to about 100 W, from about 0.5 W to about 80 W, from about 0.5 W to about 60 W, from about 0.5 W to about 40 W, from about 0.5 W to about 20 W, from about 0.5 W to about 18 W, from about 0.5 W to

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about 60 W, from about 60 W to about 100 W, from about 60 W to about 80 W, from about 80 W to about 100 W; or at most about 0.1 W, at most about 0.25 W, at most about 0.5 W, at most about 0.6 W, at most about 0.75 W, at most about 1 W, at most about 2 W, at most about 3 W, at most about 4 W, at most about 5 W, at most about 6 W, at most about 8 W, at most about 10 W, at most about 12 W, at most about 14 W, at most about 16 W, at most about 18 W, at most about 20 W, at most about 40 W, at most about 60 W, at most about 80 W, at most about 100 W; or about 0.1 W, about 0.25 W, about 0.5 W, about 0.6 W, about 0.75 W, about 1 W, about 2 W, about 3 W, about 4 W, about 5 W, about 6 W, about 8 W, about 10 W, about 12 W, about 14 W, about 16 W, about 18 W, about 20 W, about 40 W, about 60 W, about 80 W, about 100 W, or any ranges and values therebetween. In a preferred embodiment, step (c) comprises subjecting the mixture to laser irradiation at a power of from about 0.1 W to about 100 W. In another preferred embodiment, step (c) comprises subjecting the mixture to laser irradiation at a power of from about 0.1 W to about 20 W. In yet another preferred embodiment, step (c) comprises subjecting the mixture to laser irradiation at a power of from about 0.5 W to about 12 W.

Irradiating the mixture with a laser beam results in a localised heating of the area to sufficiently high peak temperatures to induce the melting and subsequent phase changes as observed in the method of the invention. In some embodiments, step (c) comprises subjecting the mixture to laser irradiation to reach peak temperatures in a range of at least about 250 °C, at least about 500 °C, at least about 750 °C, at least about 1000 °C, at least about 1250 °C, at least about 1445 °C, at least about 1500 °C, at least about 1750 °C, at least about 1768 °C, at least about 2000 °C, at least about 2250 °C, at least about 2500 °C, at least about 2750 °C, at least about 3000 °C, at least about 3165 °C, at least about 3250 °C, at least about 3500 °C, at least about 3580 °C, at least about 3590 °C, at least about 3750 °C, at least about 4000 °C; or from about 250 °C to about 4000 °C, from about 250 °C to about 3750 °C, from about 250 °C to about 3590 °C, from about 250 °C to about 3580 °C, from about 250 °C to about 3500 °C, from about 250 °C to about 3250 °C, from about 250 °C to about 3165 °C, from about 250 °C to about 3000 °C, from about 250 °C to about 2750 °C, from about 250 °C to about 2500 °C, from about 250 °C to about 2250 °C, from about 250 °C to about 2000 °C, from about 250 °C to about 1768 °C, from about 250 °C to about 1750 °C, from about 250 °C to about 1500 °C, from about 250 °C to about 1445 °C, from about 250 °C to about 1250 °C, from about 250 °C to about 1000 °C, from about 250 °C to about 750 °C, from about 250 °C to about 500 °C, from about 500 °C to about 4000 °C, from about 500 °C to about 3750 °C, from about 500 °C to about 3590 °C, from about 500 °C to about 3580 °C, from about 500 °C to about 3500 °C, from about 500 °C to about 3250 °C, from about 500 °C to about 3165 °C, from about 500 °C to about 3000 °C, from about 500 °C to about 2750 °C, from about 500 °C to about 2500 °C, from about 500 °C to about 2250 °C, from about 500 °C to about 2000 °C, from about 500 °C to about 1768 °C, from about 500 °C to about 1750 °C, from about 500 °C to about 1500 °C, from about 500 °C to about 1445 °C, from about 500 °C to about 1250 °C, from about 500 °C to about 1000 °C, from about 500 °C to about 750 °C, from about 750 °C to about 4000 °C, from about 750 °C to about 3750 °C, from about 750 °C to about 3590 °C, from about 750 °C to about 3580 °C, from about 750 °C to about 3500 °C, from about 750 °C to about 3250 °C, from about 750 °C to about 3165 °C, from about 750 °C to about 3000 °C, from about 750 °C to about 2750 °C, from about 750 °C to about 2500 °C, from about 750 °C to about 2250 °C, from about 750 °C to about 2000 °C, from about 750 °C to about 1768 °C, from about 750 °C to about 1750 °C, from about 750 °C to about 1500 °C, from about 750 °C to about 1445 °C, from about 750 °C to about 1250 °C, from about 750 °C to about 1000 °C, from about 1000 °C to about 4000 °C, from about 1000 °C to about 3750 °C, from about 1000 °C to about 3590 °C, from about 1000 °C to about 3580 °C, from about 1000 °C to about 3500 °C, from about 1000 °C to about 3250 °C, from about 1000 °C to about 3165 °C, from about 1000 °C to about 3000 °C, from about 1000 °C to about 2750 °C, from about 1000 °C to about 2500 °C, from about 1000 °C to about 2250 °C, from about 1000 °C to about 2000 °C, from about 1000 °C to about 1768 °C, from about 1000 °C to about 1750 °C, from about 1000 °C to about 1500 °C, from about 1000 °C to about 1445 °C, from about 1000 °C to about 1250 °C, from about 1250 °C to about 4000 °C, from about 1250 °C to about 3750 °C, from about 1250 °C to about 3590 °C, from about 1250 °C to about 3580 °C, from about 1250 °C to about 3500 °C, from about 1250 °C to about 3250 °C, from about 1250 °C to about 3165 °C, from about 1250 °C to about 3000 °C, from about 1250 °C to about 2750 °C, from about 1250 °C to about 2500 °C, from about 1250 °C to about 2250 °C, from about 1250 °C to about 2000 °C, from about 1250 °C to about 1768 °C, from about 1250 °C to about 1750 °C, from about 1250 °C to about 1500 °C, from about 1250 °C to about 1445 °C, from about 1445 °C to about 4000 °C, from about 1445 °C to about 3750 °C, from about 1445 °C to about 3590 °C, from about 1445 °C to about 3580 °C, from about 1445 °C to about 3500 °C, from about 1445 °C to about

3250 °C, from about 1445 °C to about 3165 °C, from about 1445 °C to about 3000 °C, from about 1445 °C to about 2750 °C, from about 1445 °C to about 2500 °C, from about 1445 °C to about 2250 °C, from about 1445 °C to about 2000 °C, from about 1445 °C to about 1768 °C, from about 1445 °C to about 1750 °C, from about 1445 °C to about 1500 °C, from about 1500 °C to about 4000 °C, from about 1500 °C to about 3750 °C, from about 1500 °C to about 3590 °C, from about 1500 °C to about 3580 °C, from about 1500 °C to about 3500 °C, from about 1500 °C to about 3250 °C, from about 1500 °C to about 3165 °C, from about 1500 °C to about 3000 °C, from about 1500 °C to about 2750 °C, from about 1500 °C to about 2500 °C, from about 1500 °C to about 2250 °C, from about 1500 °C to about 2000 °C, from about 1500 °C to about 1768 °C, from about 1500 °C to about 1750 °C, from about 1750 °C to about 4000 °C, from about 1750 °C to about 3750 °C, from about 1750 °C to about 3590 °C, from about 1750 °C to about 3580 °C, from about 1750 °C to about 3500 °C, from about 1750 °C to about 3250 °C, from about 1750 °C to about 3165 °C, from about 1750 °C to about 3000 °C, from about 1750 °C to about 2750 °C, from about 1750 °C to about 2500 °C, from about 1750 °C to about 2250 °C, from about 1750 °C to about 2000 °C, from about 1750 °C to about 1768 °C, from about 1768 °C to about 4000 °C, from about 1768 °C to about 3750 °C, from about 1768 °C to about 3590 °C, from about 1768 °C to about 3580 °C, from about 1768 °C to about 3500 °C, from about 1768 °C to about 3250 °C, from about 1768 °C to about 3165 °C, from about 1768 °C to about 3000 °C, from about 1768 °C to about 2750 °C, from about 1768 °C to about 2500 °C, from about 1768 °C to about 2250 °C, from about 1768 °C to about 2000 °C, from about 2000 °C to about 4000 °C, from about 2000 °C to about 3750 °C, from about 2000 °C to about 3590 °C, from about 2000 °C to about 3580 °C, from about 2000 °C to about 3500 °C, from about 2000 °C to about 3250 °C, from about 2000 °C to about 3165 °C, from about 2000 °C to about 3000 °C, from about 2000 °C to about 2750 °C, from about 2000 °C to about 2500 °C, from about 2000 °C to about 2250 °C, from about 2250 °C to about 4000 °C, from about 2250 °C to about 3750 °C, from about 2250 °C to about 3590 °C, from about 2250 °C to about 3580 °C, from about 2250 °C to about 3500 °C, from about 2250 °C to about 3250 °C, from about 2250 °C to about 3165 °C, from about 2250 °C to about 3000 °C, from about 2250 °C to about 2750 °C, from about 2250 °C to about 2500 °C, from about 2500 °C to about 4000 °C, from about 2500 °C to about 3750 °C, from about 2500 °C to about 3590 °C, from about 2500 °C to about 3580 °C, from about 2500 °C to about 3500 °C, from about 2500 °C to about 3250 °C, from about 2500 °C to about 3165 °C, from about 2500 °C to about 3000 °C, from about 2500 °C to about 2750 °C, from about 2750 °C to about 4000 °C, from about 2750 °C to about 3750 °C, from about 2750 °C to about 3590 °C, from about 2750 °C to about 3580 °C, from about 2750 °C to about 3500 °C, from about 2750 °C to about 3250 °C, from about 2750 °C to about 3165 °C, from about 2750 °C to about 3000 °C, from about 3000 °C to about 4000 °C, from about 3000 °C to about 3750 °C, from about 3000 °C to about 3590 °C, from about 3000 °C to about 3580 °C, from about 3000 °C to about 3500 °C, from about 3000 °C to about 3250 °C, from about 3000 °C to about 3165 °C, from about 3165 °C to about 4000 °C, from about 3165 °C to about 3750 °C, from about 3165 °C to about 3590 °C, from about 3165 °C to about 3580 °C, from about 3165 °C to about 3500 °C, from about 3165 °C to about 3250 °C, from about 3250 °C to about 4000 °C, from about 3250 °C to about 3750 °C, from about 3250 °C to about 3590 °C, from about 3250 °C to about 3580 °C, from about 3250 °C to about 3500 °C, from about 3500 °C to about 4000 °C, from about 3500 °C to about 3750 °C, from about 3500 °C to about 3590 °C, from about 3500 °C to about 3580 °C, from about 3580 °C to about 4000 °C, from about 3580 °C to about 3750 °C, from about 3580 °C to about 3590 °C, from about 3590 °C to about 4000 °C, from about 3590 °C to about 3750 °C, from about 3750 °C to about 4000 °C; or at most about 250 °C, at most about 500 °C, at most about 750 °C, at most about 1000 °C, at most about 1250 °C, at most about 1445 °C, at most about 1500 °C, at most about 1750 °C, at most about 1768 °C, at most about 2000 °C, at most about 2250 °C, at most about 2500 °C, at most about 2750 °C, at most about 3000 °C, at most about 3165 °C, at most about 3250 °C, at most about 3500 °C, at most about 3580 °C, at most about 3590 °C, at most about 3750 °C, at most about 4000 °C; or about 250 °C, about 500 °C, about 750 °C, about 1000 °C, about 1250 °C, about 1445 °C, about 1500 °C, about 1750 °C, about 1768 °C, about 2000 °C, about 2250 °C, about 2500 °C, about 2750 °C, about 3000 °C, about 3165 °C, about 3250 °C, about 3500 °C, about 3580 °C, about 3590 °C, about 3750 °C, about 4000 °C, or any ranges or values therebetween. In some preferred embodiments, step (c) comprises subjecting the mixture to laser irradiation to reach peak temperatures in the range of 250 °C to about 4000 °C. In some further preferred embodiments, step (c) comprises subjecting the mixture to laser irradiation to reach peak temperatures in the range of 1000 °C to about 4000 °C.

In some embodiments, step (c) comprises subjecting the mixture to laser irradiation for a duration of about 0.01 ms to about 500 ms, at a power of about 0.1 W to about 100 W to reach peak temperatures

of 250 to 4000 °C. In some embodiments, step (c) comprises subjecting the mixture to laser irradiation for a duration of about 0.25 ms to about 500 ms, at a power of about 0.5 W to about 12 W to reach peak temperatures of 1000 to 4000 °C.

In yet some other embodiments, step (c) comprises subjecting the mixture to laser irradiation at an average power intensity of in a range of at least about 0.25 kW/cm², at least about 0.625 kW/cm², at least about 1.25 kW/cm², at least about 1.5 kW/cm², at least about 1.875 kW/cm², at least about 2.5 kW/cm², at least about 5 kW/cm², at least about 7.5 kW/cm², at least about 10 kW/cm², at least about 12.5 kW/cm², at least about 15 kW/cm², at least about 20 kW/cm², at least about 25 kW/cm², at least about 30 kW/cm², at least about 35 kW/cm², at least about 40 kW/cm², at least about 45 kW/cm², at least about 50 kW/cm², at least about 100 kW/cm², at least about 150 kW/cm², at least about 200 kW/cm², at least about 250 kW/cm²; or from about 0.25 kW/cm² to about 250 kW/cm², from about 0.25 kW/cm² to about 200 kW/cm², from about 0.25 kW/cm² to about 150 kW/cm², from about 0.25 kW/cm² to about 100 kW/cm², from about 0.25 kW/cm² to about 50 kW/cm², from about 0.25 kW/cm² to about 45 kW/cm², from about 0.25 kW/cm² to about 40 kW/cm², from about 0.25 kW/cm² to about 35 kW/cm², from about 0.25 kW/cm² to about 30 kW/cm², from about 0.25 kW/cm² to about 25 kW/cm², from about 0.25 kW/cm² to about 20 kW/cm², from about 0.25 kW/cm² to about 15 kW/cm², from about 0.25 kW/cm² to about 12.5 kW/cm², from about 0.25 kW/cm² to about 10 kW/cm², from about 0.25 kW/cm² to about 7.5 kW/cm², from about 0.25 kW/cm² to about 5 kW/cm², from about 0.25 kW/cm² to about 2.5 kW/cm², from about 0.25 kW/cm² to about 1.875 kW/cm², from about 0.25 kW/cm² to about 1.5 kW/cm², from about 0.25 kW/cm² to about 1.25 kW/cm², from about 0.25 kW/cm² to about 0.625 kW/cm², from about 0.625 kW/cm² to about 250 kW/cm², from about 0.625 kW/cm² to about 200 kW/cm², from about 0.625 kW/cm² to about 150 kW/cm², from about 0.625 kW/cm² to about 100 kW/cm², from about 0.625 kW/cm² to about 50 kW/cm², from about 0.625 kW/cm² to about 45 kW/cm², from about 0.625 kW/cm² to about 40 kW/cm², from about 0.625 kW/cm² to about 35 kW/cm², from about 0.625 kW/cm² to about 30 kW/cm², from about 0.625 kW/cm² to about 25 kW/cm², from about 0.625 kW/cm² to about 20 kW/cm², from about 0.625 kW/cm² to about 15 kW/cm², from about 0.625 kW/cm² to about 12.5 kW/cm², from about 0.625 kW/cm² to about 10 kW/cm², from about 0.625 kW/cm² to about 7.5 kW/cm², from about 0.625 kW/cm² to about 5 kW/cm², from about 0.625 kW/cm² to about 2.5 kW/cm², from about 0.625 kW/cm² to about 1.875 kW/cm², from about 0.625 kW/cm² to about 1.5 kW/cm², from about 0.625 kW/cm² to about 1.25 kW/cm², from about 1.25 kW/cm² to about 250 kW/cm², from about 1.25 kW/cm² to about 200 kW/cm², from about 1.25 kW/cm² to about 150 kW/cm², from about 1.25 kW/cm² to about 100 kW/cm², from about 1.25 kW/cm² to about 50 kW/cm², from about 1.25 kW/cm² to about 45 kW/cm², from about 1.25 kW/cm² to about 40 kW/cm², from about 1.25 kW/cm² to about 35 kW/cm², from about 1.25 kW/cm² to about 30 kW/cm², from about 1.25 kW/cm² to about 25 kW/cm², from about 1.25 kW/cm² to about 20 kW/cm², from about 1.25 kW/cm² to about 15 kW/cm², from about 1.25 kW/cm² to about 12.5 kW/cm², from about 1.25 kW/cm² to about 10 kW/cm², from about 1.25 kW/cm² to about 7.5 kW/cm², from about 1.25 kW/cm² to about 5 kW/cm², from about 1.25 kW/cm² to about 2.5 kW/cm², from about 1.25 kW/cm² to about 1.875 kW/cm², from about 1.25 kW/cm² to about 1.5 kW/cm², from about 1.5 kW/cm² to about 250 kW/cm², from about 1.5 kW/cm² to about 200 kW/cm², from about 1.5 kW/cm² to about 150 kW/cm², from about 1.5 kW/cm² to about 100 kW/cm², from about 1.5 kW/cm² to about 50 kW/cm², from about 1.5 kW/cm² to about 45 kW/cm², from about 1.5 kW/cm² to about 40 kW/cm², from about 1.5 kW/cm² to about 35 kW/cm², from about 1.5 kW/cm² to about 30 kW/cm², from about 1.5 kW/cm² to about 25 kW/cm², from about 1.5 kW/cm² to about 20 kW/cm², from about 1.5 kW/cm² to about 15 kW/cm², from about 1.5 kW/cm² to about 12.5 kW/cm², from about 1.5 kW/cm² to about 10 kW/cm², from about 1.5 kW/cm² to about 7.5 kW/cm², from about 1.5 kW/cm² to about 5 kW/cm², from about 1.5 kW/cm² to about 2.5 kW/cm², from about 1.5 kW/cm² to about 1.875 kW/cm², from about 1.875 kW/cm² to about 250 kW/cm², from about 1.875 kW/cm² to about 200 kW/cm², from about 1.875 kW/cm² to about 150 kW/cm², from about 1.875 kW/cm² to about 100 kW/cm², from about 1.875 kW/cm² to about 50 kW/cm², from about 1.875 kW/cm² to about 45 kW/cm², from about 1.875 kW/cm² to about 40 kW/cm², from about 1.875 kW/cm² to about 35 kW/cm², from about 1.875 kW/cm² to about 30 kW/cm², from about 1.875 kW/cm² to about 25 kW/cm², from about 1.875 kW/cm² to about 20 kW/cm², from about 1.875 kW/cm² to about 15 kW/cm², from about 1.875 kW/cm² to about 12.5 kW/cm², from about 1.875 kW/cm² to about 10 kW/cm², from about 1.875 kW/cm² to about 7.5 kW/cm², from about 1.875 kW/cm² to about 5 kW/cm², from about 1.875 kW/cm² to about 2.5 kW/cm², from about 2.5 kW/cm² to about 250 kW/cm², from about 2.5 kW/cm² to about 200 kW/cm², from about 2.5 kW/cm² to about 150 kW/cm², from about 2.5 kW/cm² to about 100 kW/cm², from about

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150 kW/cm² to about 250 kW/cm², from about 150 kW/cm² to about 200 kW/cm², from about 200 kW/cm² to about 250 kW/cm²; or at most about 0.25 kW/cm², at most about 0.625 kW/cm², at most about 1.25 kW/cm², at most about 1.5 kW/cm², at most about 1.875 kW/cm², at most about 2.5 kW/cm², at most about 5 kW/cm², at most about 7.5 kW/cm², at most about 10 kW/cm², at most about 12.5 kW/cm², at most about 15 kW/cm², at most about 20 kW/cm², at most about 25 kW/cm², at most about 30 kW/cm², at most about 35 kW/cm², at most about 40 kW/cm², at most about 45 kW/cm², at most about 50 kW/cm², at most about 100 kW/cm², at most about 150 kW/cm², at most about 200 kW/cm², at most about 250 kW/cm²; or about 0.25 kW/cm², about 0.625 kW/cm², about 1.25 kW/cm², about 1.5 kW/cm², about 1.875 kW/cm², about 2.5 kW/cm², about 5 kW/cm², about 7.5 kW/cm², about 10 kW/cm², about 12.5 kW/cm², about 15 kW/cm², about 20 kW/cm², about 25 kW/cm², about 30 kW/cm², about 35 kW/cm², about 40 kW/cm², about 45 kW/cm², about 50 kW/cm², about 100 kW/cm², about 150 kW/cm², about 200 kW/cm², about 250 kW/cm², or any ranges or values therebetween.

In some other embodiments, the multiphasic crystalline nanoparticle(s) comprises phases and/or crystal systems selected from face-centered cubic (FCC), body-centered cubic (BCC), cubic rock salt, hexagonal close packing (HCP), simple cubic, diamond cubic, tetragonal, rutile tetragonal, hexagonal, orthorhombic, rhombohedral, monoclinic or triclinic crystal systems. In some embodiments, the nanoparticle may contain more than one of the same phase and/or crystal system. In some preferred embodiments, the multiphasic crystalline nanoparticle(s) comprises FCC, BCC, tetragonal rutile and cubic rock salt phases and/or crystal systems. In some further preferred embodiments, the multiphasic crystalline nanoparticle(s) comprises face-centred cubic (FCC) and/or body-centred cubic (BCC) phases and/or crystal systems. In another preferred embodiment, the multiphasic crystalline nanoparticle(s) comprises FCC1, FCC2 and BCC phases. In yet some other preferred embodiments, the multiphasic crystalline nanoparticle(s) comprises tetragonal rutile and/or cubic rock salt phases and/or crystal systems.

In some embodiments, the multiphasic crystalline nanoparticles comprise at least two phases and/or crystal systems. In some further embodiments, the multiphasic crystalline nanoparticles comprise at least three phases and/or crystal systems. In yet further embodiments, the multiphasic crystalline nanoparticles comprise at least four phases and/or crystal systems.

In some embodiments, the multiphasic crystalline nanoparticle(s) comprises at least two phases and/or crystal systems selected from the group consisting of face-centred cubic (FCC), body-centred cubic (BCC), cubic rock salt, tetragonal, rutile tetragonal, hexagonal, orthorhombic, rhombohedral, monoclinic or triclinic crystal systems. In some preferred embodiments, the multiphasic crystalline nanoparticle(s) comprises at least two phases and/or crystal systems selected from the group consisting of face-centred cubic (FCC), body-centred cubic (BCC), tetragonal rutile and cubic rock salt. In some preferred embodiments, the multiphasic crystalline nanoparticle(s) comprises at least two phases and/or crystal systems selected from tetragonal rutile and/or cubic rock salt. In some preferred embodiments, the multiphasic crystalline nanoparticle(s) comprises at least three phases and/or crystal systems selected from the group consisting of face-centred cubic (FCC), body-centred cubic (BCC). In some preferred embodiments, the multiphasic crystalline nanoparticle(s) comprises at least three phases and/or crystal systems, i.e., FCC1, FCC2 and BCC.

In the presently disclosed method, step (a) comprises preparing a mixture of solvent, and at least one metal precursor, at least two metal precursors, at least three metal precursors, at least four metal precursors, at least five metal precursors, at least six metal precursors; or from one to six metal precursors, from one to five metal precursors, from one to four metal precursors, from one to three metal precursors, from one to two metal precursors, from two to six metal precursors, from two to five metal precursors, from two to four metal precursors, from two to three metal precursors, from three to six metal precursors, from three to five metal precursors, from three to four metal precursors, from four to six metal precursors, from four to five metal precursors, from five to six metal precursors; or at most one metal precursor, at most two metal precursors, at most three metal precursors, at most four metal precursors, at most five metal precursors, at most six metal precursors; or one metal precursor, two metal precursors, three metal precursors, four metal precursors, five metal precursors, six metal precursors, or any ranges and values therebetween.

In some preferred embodiments, step (a) of the presently disclosed method comprises preparing a mixture of solvent and at least four metal precursors. In some further preferred embodiments, step (a) of the presently disclosed method comprises preparing a mixture of solvent and at least five metal precursors.

In the method of the present invention, step (a) comprises preparing a mixture of solvent and metal precursor(s) selected from metal salts, metal oxides, metal nitrates, metal chlorides, metal nitrides, metal isopropoxides, metal ethoxides, metal oxytriisopropoxides, metal bromides, metal alkoxides, metallates, and combinations thereof. In some preferred embodiments, step (a) comprises preparing a mixture of solvent and metal precursor(s) selected from metal salts, metal nitrates, metal chlorides, metal nitrides, metal isopropoxides, metal ethoxides, metal oxytriisopropoxides, metal alkoxides, metallates, and combinations thereof.

In the method of the present invention, step (a) comprises preparing a mixture of solvent and metal precursor(s), wherein the metal of the metal precursors is selected from Li, Be, Na, Mg, K, Ca, Rb, Sr, Ba, Fr, Ra, Al, Ga, Ge, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and combinations thereof. In some preferred embodiments, the metal of the metal precursors is selected from Li, Be, Na, Mg, K, Ca, Rb, Sr, Ba, Fr, Ra, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Ru, Rh, Pd, Ag, Cd, W, Re, Os, Ir, Pt, Au, Hg, Nb, Ce, Al, Cs, Si, Ge, Sn, Pb and combinations thereof.

In some preferred embodiments, the metal of the metal precursors is selected from Ag, Pd, Cu, Fe, Ni, Cr, Co, Ti, Nb, Al, Ce, V and combinations thereof. In some other preferred embodiments, the metal of the precursors is selected from Au, Pd, Cu, Fe, Ni and combinations thereof. In yet other preferred embodiments, the metal of the precursors is selected from Cr, Mn, Fe, Co, Ni and combinations thereof. In some other preferred embodiments, the metal of the precursors is selected from Cr, Fe, Co, Ni, Pd and combinations thereof. In yet other preferred embodiments, the metal of the precursors is selected from Ti, Nb, Al, Ce, V and combinations thereof. In some other preferred embodiments, the metal of the precursors is selected from Au, Cu, Co, Fe and combinations thereof. In yet other preferred embodiments, the metal of the precursors is selected from Au, Cu, Fe and combinations thereof.

In the method of the present invention, the method produces multiphasic crystalline nanoparticle(s) of AuPdCuFeNi, CrMnFeCoNi, CrFeCoNiPd, TiNbAlCeV, AuCuCoFe, AgCu or AuCuFe.

In the method of the present invention, step (a) comprises preparing a mixture of solvent and metal precursor(s), wherein the atomic sizes of the metal of the metal precursor(s) differ by a value in the range of at least about 0.5%, at least about 1%, at least about 2%, at least about 3%, at least about 4%, at least about 5%, at least about 6%, at least about 7%, at least about 8%, at least about 9%, at least about 10%, at least about 11%, at least about 12%, at least about 13%, at least about 14%, at least about 15%; or from about 0.5% to about 15%, from about 0.5% to about 14%, from about 0.5% to about 13%, from about 0.5% to about 12%, from about 0.5% to about 11%, from about 0.5% to about 10%, from about 0.5% to about 9%, from about 0.5% to about 8%, from about 0.5% to about 7%, from about 0.5% to about 6%, from about 0.5% to about 5%, from about 0.5% to about 4%, from about 0.5% to about 3%, from about 0.5% to about 2%, from about 0.5% to about 1%, from about 1% to about 15%, from about 1% to about 14%, from about 1% to about 13%, from about 1% to about 12%, from about 1% to about 11%, from about 1% to about 10%, from about 1% to about 9%, from about 1% to about 8%, from about 1% to about 7%, from about 1% to about 6%, from about 1% to about 5%, from about 1% to about 4%, from about 1% to about 3%, from about 1% to about 2%, from about 2% to about 15%, from about 2% to about 14%, from about 2% to about 13%, from about 2% to about 12%, from about 2% to about 11%, from about 2% to about 10%, from about 2% to about 9%, from about 2% to about 8%, from about 2% to about 7%, from about 2% to about 6%, from about 2% to about 5%, from about 2% to about 4%, from about 2% to about 3%, from about 3% to about 15%, from about 3% to about 14%, from about 3% to about 13%, from about 3% to about 12%, from about 3% to about 11%, from about 3% to about 10%, from about 3% to about 9%, from about 3% to about 8%, from about 3% to about 7%, from about 3% to about 6%, from about 3% to about 5%, from about 3% to about 4%, from about 4% to about 15%, from about 4% to about 14%, from about 4% to about 13%, from about 4% to about 12%, from about 4% to about 11%, from about 4% to about 10%, from about 4% to about 9%, from about 4% to about 8%, from about 4% to about 7%, from

about 4% to about 6%, from about 4% to about 5%, from about 5% to about 15%, from about 5% to about 14%, from about 5% to about 13%, from about 5% to about 12%, from about 5% to about 11%, from about 5% to about 10%, from about 5% to about 9%, from about 5% to about 8%, from about 5% to about 7%, from about 5% to about 6%, from about 6% to about 15%, from about 6% to about 14%, from about 6% to about 13%, from about 6% to about 12%, from about 6% to about 11%, from about 6% to about 10%, from about 6% to about 9%, from about 6% to about 8%, from about 6% to about 7%, from about 7% to about 15%, from about 7% to about 14%, from about 7% to about 13%, from about 7% to about 12%, from about 7% to about 11%, from about 7% to about 10%, from about 7% to about 9%, from about 7% to about 8%, from about 8% to about 15%, from about 8% to about 14%, from about 8% to about 13%, from about 8% to about 12%, from about 8% to about 11%, from about 8% to about 10%, from about 8% to about 9%, from about 9% to about 15%, from about 9% to about 14%, from about 9% to about 13%, from about 9% to about 12%, from about 9% to about 11%, from about 9% to about 10%, from about 10% to about 15%, from about 10% to about 14%, from about 10% to about 13%, from about 10% to about 12%, from about 10% to about 11%, from about 11% to about 15%, from about 11% to about 14%, from about 11% to about 13%, from about 11% to about 12%, from about 12% to about 15%, from about 12% to about 14%, from about 12% to about 13%, from about 13% to about 15%, from about 13% to about 14%, from about 14% to about 15%; or at most about 0.5%, at most about 1%, at most about 2%, at most about 3%, at most about 4%, at most about 5%, at most about 6%, at most about 7%, at most about 8%, at most about 9%, at most about 10%, at most about 11%, at most about 12%, at most about 13%, at most about 14%, at most about 15%; or about 0.5%, about 1%, about 2%, about 3%, about 4%, about 5%, about 6%, about 7%, about 8%, about 9%, about 10%, about 11%, about 12%, about 13%, about 14%, about 15%, or any other values and ranges therebetween. In a preferred embodiment, the atomic size of the metal of the metal precursors differs by about 5% to about 15%. In a further preferred embodiment, the atomic size of the metal of the metal precursors by about 8%.

In the method of the present invention, step (c) is performed with either a pulsed laser or a continuous wave laser. In some embodiments, step (c) is performed with a continuous wave laser.

In the method of the present invention, step (c) is performed with a laser having a wavelength in a range of at least about 200 nm, at least about 300 nm, at least about 400 nm, at least about 450 nm, at least about 500 nm, at least about 532 nm, at least about 550 nm, at least about 600 nm, at least about 650 nm, at least about 700 nm, at least about 1064 nm, at least about 2000 nm, at least about 3000 nm, at least about 4000 nm, at least about 5000 nm, at least about 8000 nm, at least about 10000 nm, at least about 10600 nm; or from about 200 nm to about 10600 nm, from about 200 nm to about 10000 nm, from about 200 nm to about 8000 nm, from about 200 nm to about 5000 nm, from about 200 nm to about 4000 nm, from about 200 nm to about 3000 nm, from about 200 nm to about 2000 nm, from about 200 nm to about 1064 nm, from about 200 nm to about 700 nm, from about 200 nm to about 650 nm, from about 200 nm to about 600 nm, from about 200 nm to about 550 nm, from about 200 nm to about 532 nm, from about 200 nm to about 500 nm, from about 200 nm to about 450 nm, from about 200 nm to about 400 nm, from about 200 nm to about 300 nm, from about 300 nm to about 10600 nm, from about 300 nm to about 10000 nm, from about 300 nm to about 8000 nm, from about 300 nm to about 5000 nm, from about 300 nm to about 4000 nm, from about 300 nm to about 3000 nm, from about 300 nm to about 2000 nm, from about 300 nm to about 1064 nm, from about 300 nm to about 700 nm, from about 300 nm to about 650 nm, from about 300 nm to about 600 nm, from about 300 nm to about 550 nm, from about 300 nm to about 532 nm, from about 300 nm to about 500 nm, from about 300 nm to about 450 nm, from about 300 nm to about 400 nm, from about 300 nm to about 200 nm, from about 400 nm to about 10600 nm, from about 400 nm to about 10000 nm, from about 400 nm to about 8000 nm, from about 400 nm to about 5000 nm, from about 400 nm to about 4000 nm, from about 400 nm to about 3000 nm, from about 400 nm to about 2000 nm, from about 400 nm to about 1064 nm, from about 400 nm to about 700 nm, from about 400 nm to about 650 nm, from about 400 nm to about 600 nm, from about 400 nm to about 550 nm, from about 400 nm to about 532 nm, from about 400 nm to about 500 nm, from about 400 nm to about 450 nm, from about 450 nm to about 10600 nm, from about 450 nm to about 10000 nm, from about 450 nm to about 8000 nm, from about 450 nm to about 5000 nm, from about 450 nm to about 4000 nm, from about 450 nm to about 3000 nm, from about 450 nm to about 2000 nm, from about 450 nm to about 1064 nm, from about 450 nm to about 700 nm, from about 450 nm to about 650 nm, from about 450 nm to about 600 nm, from about 450 nm to about 550 nm, from about 450 nm to about 532 nm, from about 450 nm to about 500 nm, from about 500 nm to about 10600 nm, from about 500 nm

to about 10000 nm, from about 500 nm to about 8000 nm, from about 500 nm to about 5000 nm, from about 500 nm to about 4000 nm, from about 500 nm to about 3000 nm, from about 500 nm to about 2000 nm, from about 500 nm to about 1064 nm, from about 500 nm to about 700 nm, from about 500 nm to about 650 nm, from about 500 nm to about 600 nm, from about 500 nm to about 550 nm, from about 500 nm to about 532 nm, from about 532 nm to about 10600 nm, from about 532 nm to about 10000 nm, from about 532 nm to about 8000 nm, from about 532 nm to about 5000 nm, from about 532 nm to about 4000 nm, from about 532 nm to about 3000 nm, from about 532 nm to about 2000 nm, from about 532 nm to about 1064 nm, from about 532 nm to about 700 nm, from about 532 nm to about 650 nm, from about 532 nm to about 600 nm, from about 532 nm to about 550 nm, from about 550 nm to about 10600 nm, from about 550 nm to about 10000 nm, from about 550 nm to about 8000 nm, from about 550 nm to about 5000 nm, from about 550 nm to about 4000 nm, from about 550 nm to about 3000 nm, from about 550 nm to about 2000 nm, from about 550 nm to about 1064 nm, from about 550 nm to about 700 nm, from about 550 nm to about 650 nm, from about 550 nm to about 600 nm, from about 600 nm to about 10600 nm, from about 600 nm to about 10000 nm, from about 600 nm to about 8000 nm, from about 600 nm to about 5000 nm, from about 600 nm to about 4000 nm, from about 600 nm to about 3000 nm, from about 600 nm to about 2000 nm, from about 600 nm to about 1064 nm, from about 600 nm to about 700 nm, from about 600 nm to about 650 nm, from about 650 nm to about 10600 nm, from about 650 nm to about 10000 nm, from about 650 nm to about 8000 nm, from about 650 nm to about 5000 nm, from about 650 nm to about 4000 nm, from about 650 nm to about 3000 nm, from about 650 nm to about 2000 nm, from about 650 nm to about 1064 nm, from about 650 nm to about 700 nm, from about 700 nm to about 10600 nm, from about 700 nm to about 10000 nm, from about 700 nm to about 8000 nm, from about 700 nm to about 5000 nm, from about 700 nm to about 4000 nm, from about 700 nm to about 3000 nm, from about 700 nm to about 2000 nm, from about 700 nm to about 1064 nm, from about 1064 nm to about 10600 nm, from about 1064 nm to about 10000 nm, from about 1064 nm to about 8000 nm, from about 1064 nm to about 5000 nm, from about 1064 nm to about 4000 nm, from about 1064 nm to about 3000 nm, from about 1064 nm to about 2000 nm, from about 2000 nm to about 10600 nm, from about 2000 nm to about 10000 nm, from about 2000 nm to about 8000 nm, from about 2000 nm to about 5000 nm, from about 2000 nm to about 4000 nm, from about 2000 nm to about 3000 nm, from about 3000 nm to about 10600 nm, from about 3000 nm to about 10000 nm, from about 3000 nm to about 8000 nm, from about 3000 nm to about 5000 nm, from about 3000 nm to about 4000 nm, from about 4000 nm to about 10600 nm, from about 4000 nm to about 10000 nm, from about 4000 nm to about 8000 nm, from about 4000 nm to about 5000 nm, from about 5000 nm to about 10600 nm, from about 5000 nm to about 10000 nm, from about 5000 nm to about 8000 nm, from about 8000 nm to about 10600 nm, from about 8000 nm to about 10000 nm, from about 10000 nm to about 10600 nm; or at most about 200 nm, at most about 300 nm, at most about 400 nm, at most about 450 nm, at most about 500 nm, at most about 532 nm, at most about 550 nm, at most about 600 nm, at most about 650 nm, at most about 700 nm, at most about 1064 nm, at most about 2000 nm, at most about 3000 nm, at most about 4000 nm, at most about 5000 nm, at most about 8000 nm, at most about 10000 nm, at most about 10600 nm; or about 200 nm, about 300 nm, about 400 nm, about 450 nm, about 500 nm, about 532 nm, about 550 nm, about 600 nm, about 650 nm, about 700 nm, about 1064 nm, about 2000 nm, about 3000 nm, about 4000 nm, about 5000 nm, about 8000 nm, about 10000 nm, about 10600 nm; or any ranges or values therebetween. In some preferred embodiments, step (c) is performed with a laser having a wavelength from about 400 nm to about 700 nm. In some further preferred embodiments, step (c) is performed with a 532 nm laser.

In the method of the present invention, step (c) is performed in an atmosphere selected from the group consisting of ambient air, unreactive gas, N₂, Ar, He, O₂, Ne, Kr, Rn, and mixtures thereof.

Performing the method of the present invention in an atmosphere, i.e. not a liquid medium may be useful because the atmosphere facilitates atomic diffusion and formation of alternative phases during the laser-induced melt-crystallization process. If a liquid medium is used, the metal precursors are cooled too fast and thus movement and rearrangement of the metal atoms may be hindered. Additionally, when a liquid medium is used, the selection of metal precursors that may be used is limited, for example, soluble metal salts, hygroscopic metal salts, or water-sensitive metal salts and precursors may all not be used.

Any suitable substrate that is thermally conductive may be suitable to be used with the present invention. In the method of the present invention, the substrate in step (b) comprises reduced graphene

oxide, graphene oxide, cellulose, chitosan, carbon, carbon nanofiber, silicon, glass, quartz, sapphire, and/or polyacrylonitrile.

In the method of the present invention, the concentration of the metal precursors in the mixture of step (a) is substantially equimolar. In some embodiments, the concentration of the metal precursors in the mixture of step (a) is not equimolar.

In the method of the present invention, the total concentration of the metal precursors in the mixture of step (a) is in a range of at least about 0.01 M, at least about 0.02 M, at least about 0.04 M, at least about 0.05 M, at least about 0.06 M, at least about 0.08 M, at least about 0.1 M, at least about 0.2 M, at least about 0.4 M, at least about 0.6 M, at least about 0.8 M, at least about 1 M, at least about 2 M, at least about 3 M, at least about 4 M, at least about 5 M, at least about 6 M, at least about 7 M, at least about 8 M, at least about 9 M, at least about 10 M; or from about 0.01 M to about 10 M, from about 0.01 M to about 9 M, from about 0.01 M to about 8 M, from about 0.01 M to about 7 M, from about 0.01 M to about 6 M, from about 0.01 M to about 5 M, from about 0.01 M to about 4 M, from about 0.01 M to about 3 M, from about 0.01 M to about 2 M, from about 0.01 M to about 1 M, from about 0.01 M to about 0.8 M, from about 0.01 M to about 0.6 M, from about 0.01 M to about 0.4 M, from about 0.01 M to about 0.2 M, from about 0.01 M to about 0.1 M, from about 0.01 M to about 0.08 M, from about 0.01 M to about 0.06 M, from about 0.01 M to about 0.05 M, from about 0.01 M to about 0.04 M, from about 0.01 M to about 0.02 M, from about 0.02 M to about 10 M, from about 0.02 M to about 9 M, from about 0.02 M to about 8 M, from about 0.02 M to about 7 M, from about 0.02 M to about 6 M, from about 0.02 M to about 5 M, from about 0.02 M to about 4 M, from about 0.02 M to about 3 M, from about 0.02 M to about 2 M, from about 0.02 M to about 1 M, from about 0.02 M to about 0.8 M, from about 0.02 M to about 0.6 M, from about 0.02 M to about 0.4 M, from about 0.02 M to about 0.2 M, from about 0.02 M to about 0.1 M, from about 0.02 M to about 0.08 M, from about 0.02 M to about 0.06 M, from about 0.02 M to about 0.05 M, from about 0.02 M to about 0.04 M, from about 0.04 M to about 10 M, from about 0.04 M to about 9 M, from about 0.04 M to about 8 M, from about 0.04 M to about 7 M, from about 0.04 M to about 6 M, from about 0.04 M to about 5 M, from about 0.04 M to about 4 M, from about 0.04 M to about 3 M, from about 0.04 M to about 2 M, from about 0.04 M to about 1 M, from about 0.04 M to about 0.8 M, from about 0.04 M to about 0.6 M, from about 0.04 M to about 0.4 M, from about 0.04 M to about 0.2 M, from about 0.04 M to about 0.1 M, from about 0.04 M to about 0.08 M, from about 0.04 M to about 0.06 M, from about 0.04 M to about 0.05 M, from about 0.05 M to about 10 M, from about 0.05 M to about 9 M, from about 0.05 M to about 8 M, from about 0.05 M to about 7 M, from about 0.05 M to about 6 M, from about 0.05 M to about 5 M, from about 0.05 M to about 4 M, from about 0.05 M to about 3 M, from about 0.05 M to about 2 M, from about 0.05 M to about 1 M, from about 0.05 M to about 0.8 M, from about 0.05 M to about 0.6 M, from about 0.05 M to about 0.4 M, from about 0.05 M to about 0.2 M, from about 0.05 M to about 0.1 M, from about 0.05 M to about 0.08 M, from about 0.05 M to about 0.06 M, from about 0.06 M to about 10 M, from about 0.06 M to about 9 M, from about 0.06 M to about 8 M, from about 0.06 M to about 7 M, from about 0.06 M to about 6 M, from about 0.06 M to about 5 M, from about 0.06 M to about 4 M, from about 0.06 M to about 3 M, from about 0.06 M to about 2 M, from about 0.06 M to about 1 M, from about 0.06 M to about 0.8 M, from about 0.06 M to about 0.6 M, from about 0.06 M to about 0.4 M, from about 0.06 M to about 0.2 M, from about 0.06 M to about 0.1 M, from about 0.06 M to about 0.08 M, from about 0.08 M to about 10 M, from about 0.08 M to about 9 M, from about 0.08 M to about 8 M, from about 0.08 M to about 7 M, from about 0.08 M to about 6 M, from about 0.08 M to about 5 M, from about 0.08 M to about 4 M, from about 0.08 M to about 3 M, from about 0.08 M to about 2 M, from about 0.08 M to about 1 M, from about 0.08 M to about 0.8 M, from about 0.08 M to about 0.6 M, from about 0.08 M to about 0.4 M, from about 0.08 M to about 0.2 M, from about 0.08 M to about 0.1 M, from about 0.1 M to about 10 M, from about 0.1 M to about 9 M, from about 0.1 M to about 8 M, from about 0.1 M to about 7 M, from about 0.1 M to about 6 M, from about 0.1 M to about 5 M, from about 0.1 M to about 4 M, from about 0.1 M to about 3 M, from about 0.1 M to about 2 M, from about 0.1 M to about 1 M, from about 0.1 M to about 0.8 M, from about 0.1 M to about 0.6 M, from about 0.1 M to about 0.4 M, from about 0.1 M to about 0.2 M, from about 0.2 M to about 10 M, from about 0.2 M to about 9 M, from about 0.2 M to about 8 M, from about 0.2 M to about 7 M, from about 0.2 M to about 6 M, from about 0.2 M to about 5 M, from about 0.2 M to about 4 M, from about 0.2 M to about 3 M, from about 0.2 M to about 2 M, from about 0.2 M to about 1 M, from about 0.2 M to about 0.8 M, from about 0.2 M to about 0.6 M, from about 0.2 M to about 0.4 M, from about 0.4 M to about 10 M, from about 0.4 M to about 9 M, from

about 0.4 M to about 8 M, from about 0.4 M to about 7 M, from about 0.4 M to about 6 M, from about 0.4 M to about 5 M, from about 0.4 M to about 4 M, from about 0.4 M to about 3 M, from about 0.4 M to about 2 M, from about 0.4 M to about 1 M, from about 0.4 M to about 0.8 M, from about 0.4 M to about 0.6 M, from about 0.6 M to about 10 M, from about 0.6 M to about 9 M, from about 0.6 M to about 8 M, from about 0.6 M to about 7 M, from about 0.6 M to about 6 M, from about 0.6 M to about 5 M, from about 0.6 M to about 4 M, from about 0.6 M to about 3 M, from about 0.6 M to about 2 M, from about 0.6 M to about 1 M, from about 0.6 M to about 0.8 M, from about 0.8 M to about 10 M, from about 0.8 M to about 9 M, from about 0.8 M to about 8 M, from about 0.8 M to about 7 M, from about 0.8 M to about 6 M, from about 0.8 M to about 5 M, from about 0.8 M to about 4 M, from about 0.8 M to about 3 M, from about 0.8 M to about 2 M, from about 0.8 M to about 1 M, from about 1 M to about 10 M, from about 1 M to about 9 M, from about 1 M to about 8 M, from about 1 M to about 7 M, from about 1 M to about 6 M, from about 1 M to about 5 M, from about 1 M to about 4 M, from about 1 M to about 3 M, from about 1 M to about 2 M, from about 2 M to about 10 M, from about 2 M to about 9 M, from about 2 M to about 8 M, from about 2 M to about 7 M, from about 2 M to about 6 M, from about 2 M to about 5 M, from about 2 M to about 4 M, from about 2 M to about 3 M, from about 3 M to about 10 M, from about 3 M to about 9 M, from about 3 M to about 8 M, from about 3 M to about 7 M, from about 3 M to about 6 M, from about 3 M to about 5 M, from about 3 M to about 4 M, from about 4 M to about 10 M, from about 4 M to about 9 M, from about 4 M to about 8 M, from about 4 M to about 7 M, from about 4 M to about 6 M, from about 4 M to about 5 M, from about 5 M to about 10 M, from about 5 M to about 9 M, from about 5 M to about 8 M, from about 5 M to about 7 M, from about 5 M to about 6 M, from about 6 M to about 10 M, from about 6 M to about 9 M, from about 6 M to about 8 M, from about 6 M to about 7 M, from about 7 M to about 10 M, from about 7 M to about 9 M, from about 7 M to about 8 M, from about 8 M to about 10 M, from about 8 M to about 9 M, from about 9 M to about 10 M; or at most about 0.01 M, at most about 0.02 M, at most about 0.04 M, at most about 0.05 M, at most about 0.06 M, at most about 0.08 M, at most about 0.1 M, at most about 0.2 M, at most about 0.4 M, at most about 0.6 M, at most about 0.8 M, at most about 1 M, at most about 2 M, at most about 3 M, at most about 4 M, at most about 5 M, at most about 6 M, at most about 7 M, at most about 8 M, at most about 9 M, at most about 10 M; or about 0.01 M, about 0.02 M, about 0.04 M, about 0.05 M, about 0.06 M, about 0.08 M, about 0.1 M, about 0.2 M, about 0.4 M, about 0.6 M, about 0.8 M, about 1 M, about 2 M, about 3 M, about 4 M, about 5 M, about 6 M, about 7 M, about 8 M, about 9 M, about 10 M, or any ranges or values therebetween. In some preferred embodiments, the concentration of each metal precursor in the mixture of step (a) is from about 0.01 M to about 10 M. In some preferred embodiments, the concentration of each metal precursor in the mixture of step (a) is from about 0.01 M to about 1 M. In some other preferred embodiments, the concentration of each metal precursor in the mixture of step (a) is from about 0.01 M to about 0.05 M. In some further preferred embodiments, the concentration of each metal precursor in the mixture of step (a) is about 0.05 M.

In the method of the present invention, the solvent in step (a) is selected from the group consisting of water, alcohols, ketones, ethers, amides, lactones, lactams, sulfones, sulfoxides, alkanes, alkenes, and combinations thereof.

In the method of the present invention, step (b) comprises dropcasting the mixture onto the substrate or immersing the substrate in the mixture. In a preferred embodiment, step (b) comprises dropcasting the mixture onto the substrate.

The present invention discloses a method, comprising:

- a. preparing a mixture of at least two metal precursors selected from the group consisting of salts, oxides, nitrates and/or alkoxides of Au, Pd, Cu, Fe, Ni, Ti, Nb, Al, Ce, V, Cr, Mn, Co, Cs, Si, Ge, Sn, and Pb;
 - b. applying the mixture to a substrate; and
 - c. subjecting the mixture to laser irradiation for a duration of about 0.25 ms to about 500 ms, at a power of about 0.5 W to about 12 W to reach peak temperatures of about 1000 °C to about 4000 °C,
- wherein step (c) comprises laser irradiating a mixture which does not comprise pure metal.

The present invention provides for a multiphasic crystalline nanoparticle comprising at least four metals selected from the group consisting of Li, Be, Na, Mg, K, Ca, Rb, Sr, Ba, Fr, Ra, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Ru, Rh, Pd, Ag, Cd, W, Re, Os, Ir, Pt, Au, Hg, Nb, Ce, Al, Cs, Si, Ge, Sn, Pb and combinations thereof, and at least two phases/and or crystal structures selected from the group consisting of FCC, BCC, cubic rock salt, tetragonal, rutile tetragonal, hexagonal, orthorhombic, rhombohedral, monoclinic or triclinic crystal systems.

The present disclosure also provides for a multiphasic crystalline nanoparticle, wherein the nanoparticle has an average particle diameter in a range of at least about 0.5 nm, at least about 1 nm, at least about 2 nm, at least about 3 nm, at least about 4 nm, at least about 5 nm, at least about 5.3 nm, at least about 8 nm, at least about 10 nm, at least about 12.6 nm, at least about 13 nm, at least about 13.8 nm, at least about 14 nm, at least about 15 nm, at least about 17 nm, at least about 20 nm, at least about 20.7 nm, at least about 21 nm, at least about 25 nm, at least about 28 nm, at least about 30 nm, at least about 35 nm, at least about 40 nm, at least about 42.4 nm, at least about 44 nm, at least about 48 nm, at least about 50 nm, at least about 53 nm, at least about 55 nm, at least about 58 nm, at least about 60 nm, at least about 62 nm, at least about 70 nm, at least about 80 nm, at least about 99.1 nm, at least about 100 nm, at least about 109 nm, at least about 120 nm, at least about 138 nm, at least about 150 nm, at least about 170 nm, at least about 196 nm, at least about 200 nm, at least about 228 nm, at least about 250 nm, at least about 260 nm, at least about 270 nm, at least about 300 nm, at least about 320 nm, at least about 340 nm, at least about 360 nm, at least about 380 nm, at least about 400 nm, at least about 420 nm, at least about 440 nm, at least about 460 nm, at least about 480 nm, at least about 500 nm; or from about 0.5 nm to about 500 nm, from about 0.5 nm to about 480 nm, from about 0.5 nm to about 460 nm, from about 0.5 nm to about 440 nm, from about 0.5 nm to about 420 nm, from about 0.5 nm to about 400 nm, from about 0.5 nm to about 380 nm, from about 0.5 nm to about 360 nm, from about 0.5 nm to about 340 nm, from about 0.5 nm to about 320 nm, from about 0.5 nm to about 300 nm, from about 0.5 nm to about 270 nm, from about 0.5 nm to about 260 nm, from about 0.5 nm to about 250 nm, from about 0.5 nm to about 228 nm, from about 0.5 nm to about 200 nm, from about 0.5 nm to about 196 nm, from about 0.5 nm to about 170 nm, from about 0.5 nm to about 150 nm, from about 0.5 nm to about 138 nm, from about 0.5 nm to about 120 nm, from about 0.5 nm to about 109 nm, from about 0.5 nm to about 100 nm, from about 0.5 nm to about 99.1 nm, from about 0.5 nm to about 80 nm, from about 0.5 nm to about 70 nm, from about 0.5 nm to about 62 nm, from about 0.5 nm to about 60 nm, from about 0.5 nm to about 58 nm, from about 0.5 nm to about 55 nm, from about 0.5 nm to about 53 nm, from about 0.5 nm to about 50 nm, from about 0.5 nm to about 48 nm, from about 0.5 nm to about 44 nm, from about 0.5 nm to about 42.4 nm, from about 0.5 nm to about 40 nm, from about 0.5 nm to about 35 nm, from about 0.5 nm to about 30 nm, from about 0.5 nm to about 28 nm, from about 0.5 nm to about 25 nm, from about 0.5 nm to about 21 nm, from about 0.5 nm to about 20.7 nm, from about 0.5 nm to about 20 nm, from about 0.5 nm to about 17 nm, from about 0.5 nm to about 15 nm, from about 0.5 nm to about 14 nm, from about 0.5 nm to about 13.8 nm, from about 0.5 nm to about 13 nm, from about 0.5 nm to about 12.6 nm, from about 0.5 nm to about 10 nm, from about 0.5 nm to about 8 nm, from about 0.5 nm to about 5.3 nm, from about 0.5 nm to about 5 nm, from about 0.5 nm to about 4 nm, from about 0.5 nm to about 3 nm, from about 0.5 nm to about 2 nm, from about 0.5 nm to about 1 nm, from about 1 nm to about 500 nm, from about 1 nm to about 480 nm, from about 1 nm to about 460 nm, from about 1 nm to about 440 nm, from about 1 nm to about 420 nm, from about 1 nm to about 400 nm, from about 1 nm to about 380 nm, from about 1 nm to about 360 nm, from about 1 nm to about 340 nm, from about 1 nm to about 320 nm, from about 1 nm to about 300 nm, from about 1 nm to about 270 nm, from about 1 nm to about 260 nm, from about 1 nm to about 250 nm, from about 1 nm to about 228 nm, from about 1 nm to about 200 nm, from about 1 nm to about 196 nm, from about 1 nm to about 170 nm, from about 1 nm to about 150 nm, from about 1 nm to about 138 nm, from about 1 nm to about 120 nm, from about 1 nm to about 109 nm, from about 1 nm to about 100 nm, from about 1 nm to about 99.1 nm, from about 1 nm to about 80 nm, from about 1 nm to about 70 nm, from about 1 nm to about 62 nm, from about 1 nm to about 60 nm, from about 1 nm to about 58 nm, from about 1 nm to about 55 nm, from about 1 nm to about 53 nm, from about 1 nm to about 50 nm, from about 1 nm to about 48 nm, from about 1 nm to about 44 nm, from about 1 nm to about 42.4 nm, from about 1 nm to about 40 nm, from about 1 nm to about 35 nm, from about 1 nm to about 30 nm, from about 1 nm to about 28 nm, from about 1 nm to about 25 nm, from about 1 nm to about 21 nm, from about 1 nm to about 20.7 nm, from about 1 nm to about 20 nm, from about 1 nm to about 17 nm, from about 1 nm to about 15 nm, from about 1 nm to about 14 nm, from about 1 nm to about 13.8 nm, from about 1 nm to about 13 nm, from about 1 nm to about 12.6 nm, from about 1 nm to about 10 nm, from about 1 nm to about 8 nm, from about 1 nm to about 5.3 nm, from about 1 nm to about 5 nm, from about 1 nm to about 4 nm, from about 1 nm to about 3 nm, from about 1 nm to about 2 nm, from about 1 nm to about 1 nm.

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nm to about 260 nm, from about 260 nm to about 500 nm, from about 260 nm to about 480 nm, from about 260 nm to about 460 nm, from about 260 nm to about 440 nm, from about 260 nm to about 420 nm, from about 260 nm to about 400 nm, from about 260 nm to about 380 nm, from about 260 nm to about 360 nm, from about 260 nm to about 340 nm, from about 260 nm to about 320 nm, from about 260 nm to about 300 nm, from about 260 nm to about 270 nm, from about 270 nm to about 500 nm, from about 270 nm to about 480 nm, from about 270 nm to about 460 nm, from about 270 nm to about 440 nm, from about 270 nm to about 420 nm, from about 270 nm to about 400 nm, from about 270 nm to about 380 nm, from about 270 nm to about 360 nm, from about 270 nm to about 340 nm, from about 270 nm to about 320 nm, from about 270 nm to about 300 nm, from about 300 nm to about 500 nm, from about 300 nm to about 480 nm, from about 300 nm to about 460 nm, from about 300 nm to about 440 nm, from about 300 nm to about 420 nm, from about 300 nm to about 400 nm, from about 300 nm to about 380 nm, from about 300 nm to about 360 nm, from about 300 nm to about 340 nm, from about 300 nm to about 320 nm, from about 320 nm to about 500 nm, from about 320 nm to about 480 nm, from about 320 nm to about 460 nm, from about 320 nm to about 440 nm, from about 320 nm to about 420 nm, from about 320 nm to about 400 nm, from about 320 nm to about 380 nm, from about 320 nm to about 360 nm, from about 320 nm to about 340 nm, from about 340 nm to about 500 nm, from about 340 nm to about 480 nm, from about 340 nm to about 460 nm, from about 340 nm to about 440 nm, from about 340 nm to about 420 nm, from about 340 nm to about 400 nm, from about 340 nm to about 380 nm, from about 340 nm to about 360 nm, from about 340 nm to about 300 nm, from about 360 nm to about 480 nm, from about 360 nm to about 460 nm, from about 360 nm to about 440 nm, from about 360 nm to about 420 nm, from about 360 nm to about 400 nm, from about 360 nm to about 380 nm, from about 380 nm to about 500 nm, from about 380 nm to about 480 nm, from about 380 nm to about 460 nm, from about 380 nm to about 440 nm, from about 380 nm to about 420 nm, from about 380 nm to about 400 nm, from about 400 nm to about 500 nm, from about 400 nm to about 480 nm, from about 400 nm to about 460 nm, from about 400 nm to about 440 nm, from about 400 nm to about 420 nm, from about 420 nm to about 500 nm, from about 420 nm to about 480 nm, from about 420 nm to about 460 nm, from about 420 nm to about 440 nm, from about 440 nm to about 500 nm, from about 440 nm to about 480 nm, from about 440 nm to about 460 nm, from about 460 nm to about 500 nm, from about 460 nm to about 480 nm, from about 480 nm to about 500 nm; or at most about 0.5 nm, at most about 1 nm, at most about 2 nm, at most about 3 nm, at most about 4 nm, at most about 5 nm, at most about 5.3 nm, at most about 8 nm, at most about 10 nm, at most about 12.6 nm, at most about 13 nm, at most about 13.8 nm, at most about 14 nm, at most about 15 nm, at most about 17 nm, at most about 20 nm, at most about 20.7 nm, at most about 21 nm, at most about 25 nm, at most about 28 nm, at most about 30 nm, at most about 35 nm, at most about 40 nm, at most about 42.4 nm, at most about 44 nm, at most about 48 nm, at most about 50 nm, at most about 53 nm, at most about 55 nm, at most about 58 nm, at most about 60 nm, at most about 62 nm, at most about 70 nm, at most about 80 nm, at most about 99.1 nm, at most about 100 nm, at most about 109 nm, at most about 120 nm, at most about 138 nm, at most about 150 nm, at most about 170 nm, at most about 196 nm, at most about 200 nm, at most about 228 nm, at most about 250 nm, at most about 260 nm, at most about 270 nm, at most about 300 nm, at most about 320 nm, at most about 340 nm, at most about 360 nm, at most about 380 nm, at most about 400 nm, at most about 420 nm, at most about 440 nm, at most about 460 nm, at most about 480 nm, at most about 500 nm; or about 0.5 nm, about 1 nm, about 2 nm, about 3 nm, about 4 nm, about 5 nm, about 5.3 nm, about 8 nm, about 10 nm, about 12.6 nm, about 13 nm, about 13.8 nm, about 14 nm, about 15 nm, about 17 nm, about 20 nm, about 20.7 nm, about 21 nm, about 25 nm, about 28 nm, about 30 nm, about 35 nm, about 40 nm, about 42.4 nm, about 44 nm, about 48 nm, about 50 nm, about 53 nm, about 55 nm, about 58 nm, about 60 nm, about 62 nm, about 70 nm, about 80 nm, about 99.1 nm, about 100 nm, about 109 nm, about 120 nm, about 138 nm, about 150 nm, about 170 nm, about 196 nm, about 200 nm, about 228 nm, about 250 nm, about 260 nm, about 270 nm, about 300 nm, about 320 nm, about 340 nm, about 360 nm, about 380 nm, about 400 nm, about 420 nm, about 440 nm, about 460 nm, about 480 nm, about 500 nm, or any ranges or values therebetween. In some preferred embodiments, the nanoparticle has an average particle diameter from about 3 nm to about 500 nm. In some further preferred embodiments, the nanoparticle has an average particle diameter from about 3 nm to about 200 nm.

In some other preferred embodiments, the nanoparticle has an average particle diameter in a range of at least about 13.8 ± 1.2 nm, at least about 14 ± 1 nm, at least about 28 ± 7 nm, at least about 53 ± 9 nm, at least about 109 ± 29 nm, at least about 228 ± 32 nm; or from about 13.8 ± 1.2 nm to about 228 ± 32 nm, from about 13.8 ± 1.2 nm to about 109 ± 29 nm, from about 13.8 ± 1.2 nm to about 53 ± 9 nm, from about

13.8 ± 1.2 nm to about 28 ± 7 nm, from about 13.8 ± 1.2 nm to about 14 ± 1 nm, from about 14 ± 1 nm to about 228 ± 32 nm, from about 14 ± 1 nm to about 109 ± 29 nm, from about 14 ± 1 nm to about 53 ± 9 nm, from about 14 ± 1 nm to about 28 ± 7 nm, from about 28 ± 7 nm to about 228 ± 32 nm, from about 28 ± 7 nm to about 109 ± 29 nm, from about 28 ± 7 nm to about 53 ± 9 nm, from about 53 ± 9 nm to about 228 ± 32 nm, from about 53 ± 9 nm to about 109 ± 29 nm, from about 109 ± 29 nm to about 228 ± 32 nm; or at most about 13.8 ± 1.2 nm, at most about 14 ± 1 nm, at most about 28 ± 7 nm, at most about 53 ± 9 nm, at most about 109 ± 29 nm, at most about 228 ± 32 nm; or about 13.8 ± 1.2 nm, about 14 ± 1 nm, about 28 ± 7 nm, about 53 ± 9 nm, about 109 ± 29 nm, about 228 ± 32 nm, or any ranges or values therebetween.

The present disclosure also provides for a multiphasic crystalline nanoparticle, wherein the nanoparticle has an average lattice spacing in a range of at least about 0.1 nm, at least about 0.15 nm, at least about 0.18 nm, at least about 0.2 nm, at least about 0.20269 nm, at least about 0.203 nm, at least about 0.20604 nm, at least about 0.2088 nm, at least about 0.22 nm, at least about 0.2228 nm, at least about 0.20352 nm, at least about 0.2355 nm, at least about 0.2359 nm, at least about 0.24 nm, at least about 0.256 nm, at least about 0.26 nm, at least about 0.28 nm, at least about 0.3 nm, at least about 0.35 nm, at least about 0.4 nm, at least about 0.5 nm; or from about 0.1 nm to about 0.5 nm, from about 0.1 nm to about 0.4 nm, from about 0.1 nm to about 0.35 nm, from about 0.1 nm to about 0.3 nm, from about 0.1 nm to about 0.28 nm, from about 0.1 nm to about 0.26 nm, from about 0.1 nm to about 0.256 nm, from about 0.1 nm to about 0.24 nm, from about 0.1 nm to about 0.2359 nm, from about 0.1 nm to about 0.2355 nm, from about 0.1 nm to about 0.20352 nm, from about 0.1 nm to about 0.2228 nm, from about 0.1 nm to about 0.22 nm, from about 0.1 nm to about 0.2088 nm, from about 0.1 nm to about 0.20604 nm, from about 0.1 nm to about 0.203 nm, from about 0.1 nm to about 0.20269 nm, from about 0.1 nm to about 0.2 nm, from about 0.1 nm to about 0.18 nm, from about 0.1 nm to about 0.15 nm, from about 0.15 nm to about 0.5 nm, from about 0.15 nm to about 0.4 nm, from about 0.15 nm to about 0.35 nm, from about 0.15 nm to about 0.3 nm, from about 0.15 nm to about 0.28 nm, from about 0.15 nm to about 0.26 nm, from about 0.15 nm to about 0.256 nm, from about 0.15 nm to about 0.24 nm, from about 0.15 nm to about 0.2359 nm, from about 0.15 nm to about 0.2355 nm, from about 0.15 nm to about 0.20352 nm, from about 0.15 nm to about 0.2228 nm, from about 0.15 nm to about 0.22 nm, from about 0.15 nm to about 0.2088 nm, from about 0.15 nm to about 0.20604 nm, from about 0.15 nm to about 0.203 nm, from about 0.15 nm to about 0.20269 nm, from about 0.15 nm to about 0.2 nm, from about 0.15 nm to about 0.18 nm, from about 0.15 nm to about 0.15 nm, from about 0.18 nm to about 0.5 nm, from about 0.18 nm to about 0.4 nm, from about 0.18 nm to about 0.35 nm, from about 0.18 nm to about 0.3 nm, from about 0.18 nm to about 0.28 nm, from about 0.18 nm to about 0.26 nm, from about 0.18 nm to about 0.256 nm, from about 0.18 nm to about 0.24 nm, from about 0.18 nm to about 0.2359 nm, from about 0.18 nm to about 0.2355 nm, from about 0.18 nm to about 0.20352 nm, from about 0.18 nm to about 0.2228 nm, from about 0.18 nm to about 0.22 nm, from about 0.18 nm to about 0.2088 nm, from about 0.18 nm to about 0.20604 nm, from about 0.18 nm to about 0.203 nm, from about 0.18 nm to about 0.20269 nm, from about 0.18 nm to about 0.2 nm, from about 0.2 nm to about 0.5 nm, from about 0.2 nm to about 0.4 nm, from about 0.2 nm to about 0.35 nm, from about 0.2 nm to about 0.3 nm, from about 0.2 nm to about 0.28 nm, from about 0.2 nm to about 0.26 nm, from about 0.2 nm to about 0.256 nm, from about 0.2 nm to about 0.24 nm, from about 0.2 nm to about 0.2359 nm, from about 0.2 nm to about 0.2355 nm, from about 0.2 nm to about 0.20352 nm, from about 0.2 nm to about 0.2228 nm, from about 0.2 nm to about 0.22 nm, from about 0.2 nm to about 0.2088 nm, from about 0.2 nm to about 0.20604 nm, from about 0.2 nm to about 0.203 nm, from about 0.203 nm to about 0.5 nm, from about 0.203 nm to about 0.4 nm, from about 0.203 nm to about 0.35 nm, from about 0.203 nm to about 0.3 nm, from about 0.203 nm to about 0.28 nm, from about 0.203 nm to about 0.26 nm, from about 0.203 nm to about 0.256 nm, from about 0.203 nm to about 0.24 nm, from about 0.203 nm to about 0.2359 nm, from about 0.203 nm to about 0.2355 nm, from about 0.203 nm to about 0.20352 nm, from about 0.203 nm to about 0.2228 nm, from about 0.203 nm to about 0.22 nm, from about 0.203 nm to about 0.2088 nm, from about 0.203 nm to about 0.20604 nm, from about 0.203 nm to about 0.203 nm.

nm to about 0.20604 nm, from about 0.20604 nm to about 0.5 nm, from about 0.20604 nm to about 0.4 nm, from about 0.20604 nm to about 0.35 nm, from about 0.20604 nm to about 0.3 nm, from about 0.20604 nm to about 0.28 nm, from about 0.20604 nm to about 0.26 nm, from about 0.20604 nm to about 0.256 nm, from about 0.20604 nm to about 0.24 nm, from about 0.20604 nm to about 0.2359 nm, from about 0.20604 nm to about 0.2355 nm, from about 0.20604 nm to about 0.20352 nm, from about 0.20604 nm to about 0.2228 nm, from about 0.20604 nm to about 0.22 nm, from about 0.20604 nm to about 0.2088 nm, from about 0.2088 nm to about 0.5 nm, from about 0.2088 nm to about 0.4 nm, from about 0.2088 nm to about 0.35 nm, from about 0.2088 nm to about 0.3 nm, from about 0.2088 nm to about 0.28 nm, from about 0.2088 nm to about 0.26 nm, from about 0.2088 nm to about 0.256 nm, from about 0.2088 nm to about 0.24 nm, from about 0.2088 nm to about 0.2359 nm, from about 0.2088 nm to about 0.2355 nm, from about 0.2088 nm to about 0.20352 nm, from about 0.2088 nm to about 0.2228 nm, from about 0.2088 nm to about 0.22 nm, from about 0.22 nm to about 0.5 nm, from about 0.22 nm to about 0.4 nm, from about 0.22 nm to about 0.35 nm, from about 0.22 nm to about 0.3 nm, from about 0.22 nm to about 0.28 nm, from about 0.22 nm to about 0.26 nm, from about 0.22 nm to about 0.256 nm, from about 0.22 nm to about 0.24 nm, from about 0.22 nm to about 0.2359 nm, from about 0.22 nm to about 0.2355 nm, from about 0.22 nm to about 0.20352 nm, from about 0.22 nm to about 0.2228 nm, from about 0.2228 nm to about 0.5 nm, from about 0.2228 nm to about 0.4 nm, from about 0.2228 nm to about 0.35 nm, from about 0.2228 nm to about 0.3 nm, from about 0.2228 nm to about 0.28 nm, from about 0.2228 nm to about 0.26 nm, from about 0.2228 nm to about 0.256 nm, from about 0.2228 nm to about 0.24 nm, from about 0.2228 nm to about 0.2359 nm, from about 0.2228 nm to about 0.2355 nm, from about 0.2228 nm to about 0.20352 nm, from about 0.20352 nm to about 0.5 nm, from about 0.20352 nm to about 0.4 nm, from about 0.20352 nm to about 0.35 nm, from about 0.20352 nm to about 0.3 nm, from about 0.20352 nm to about 0.28 nm, from about 0.20352 nm to about 0.26 nm, from about 0.20352 nm to about 0.256 nm, from about 0.20352 nm to about 0.24 nm, from about 0.20352 nm to about 0.2359 nm, from about 0.20352 nm to about 0.2355 nm, from about 0.2355 nm to about 0.5 nm, from about 0.2355 nm to about 0.4 nm, from about 0.2355 nm to about 0.35 nm, from about 0.2355 nm to about 0.3 nm, from about 0.2355 nm to about 0.28 nm, from about 0.2355 nm to about 0.26 nm, from about 0.2355 nm to about 0.256 nm, from about 0.2355 nm to about 0.24 nm, from about 0.2355 nm to about 0.2359 nm, from about 0.2359 nm to about 0.5 nm, from about 0.2359 nm to about 0.4 nm, from about 0.2359 nm to about 0.35 nm, from about 0.2359 nm to about 0.3 nm, from about 0.2359 nm to about 0.28 nm, from about 0.2359 nm to about 0.26 nm, from about 0.2359 nm to about 0.256 nm, from about 0.2359 nm to about 0.24 nm, from about 0.24 nm to about 0.5 nm, from about 0.24 nm to about 0.4 nm, from about 0.24 nm to about 0.35 nm, from about 0.24 nm to about 0.3 nm, from about 0.24 nm to about 0.28 nm, from about 0.24 nm to about 0.26 nm, from about 0.24 nm to about 0.256 nm, from about 0.256 nm to about 0.5 nm, from about 0.256 nm to about 0.4 nm, from about 0.256 nm to about 0.35 nm, from about 0.256 nm to about 0.3 nm, from about 0.256 nm to about 0.28 nm, from about 0.256 nm to about 0.26 nm, from about 0.26 nm to about 0.5 nm, from about 0.26 nm to about 0.4 nm, from about 0.26 nm to about 0.35 nm, from about 0.26 nm to about 0.3 nm, from about 0.26 nm to about 0.28 nm, from about 0.28 nm to about 0.5 nm, from about 0.28 nm to about 0.4 nm, from about 0.28 nm to about 0.35 nm, from about 0.28 nm to about 0.3 nm, from about 0.3 nm to about 0.5 nm, from about 0.3 nm to about 0.4 nm, from about 0.3 nm to about 0.35 nm, from about 0.35 nm to about 0.5 nm, from about 0.35 nm to about 0.4 nm, from about 0.4 nm to about 0.5 nm; or at most about 0.1 nm, at most about 0.15 nm, at most about 0.18 nm, at most about 0.2 nm, at most about 0.20269 nm, at most about 0.203 nm, at most about 0.20604 nm, at most about 0.2088 nm, at most about 0.22 nm, at most about 0.2228 nm, at most about 0.20352 nm, at most about 0.2355 nm, at most about 0.2359 nm, at most about 0.24 nm, at most about 0.256 nm, at most about 0.26 nm, at most about 0.28 nm, at most about 0.3 nm, at most about 0.35 nm, at most about 0.4 nm, at most about 0.5 nm; or about 0.1 nm, about 0.15 nm, about 0.18 nm, about 0.2 nm, about 0.20269 nm, about 0.203 nm, about 0.20604 nm, about 0.2088 nm, about 0.22 nm, about 0.2228 nm, about 0.20352 nm, about 0.2355 nm, about 0.2359 nm, about 0.24 nm, about 0.256 nm, about 0.26 nm, about 0.28 nm, about 0.3 nm, about 0.35 nm, about 0.4 nm, about 0.5 nm; or any ranges or values therebetween. In some preferred embodiments, the nanoparticle has an average lattice spacing from about 0.1 nm to about 0.5 nm. In some further preferred embodiments, the nanoparticle has an average lattice spacing from about 0.18 nm to about 0.3 nm.

The present disclosure also provides for a multiphasic crystalline nanoparticle, wherein the nanoparticle has an average lattice constant in a range of about 0.1 nm to about 0.9 nm, about 0.15 nm to about 0.9 nm, about 0.2 nm to about 0.9 nm, about 0.25 nm to about 0.9 nm, about 0.3 nm to about 0.9 nm,

about 0.35 nm to about 0.9 nm, about 0.4 nm to about 0.9 nm, about 0.45 nm to about 0.9 nm, about 0.5 nm to about 0.9 nm, about 0.55 nm to about 0.9 nm, about 0.6 nm to about 0.9 nm, about 0.65 nm to about 0.9 nm, about 0.7 nm to about 0.9 nm, about 0.75 nm to about 0.9 nm, about 0.8 nm to about 0.9 nm, about 0.85 nm to about 0.9 nm, about 0.1 nm to about 0.85 nm, about 0.1 nm to about 0.8 nm, about 0.1 nm to about 0.75 nm, about 0.1 nm to about 0.7 nm, about 0.1 nm to about 0.65 nm, about 0.1 nm to about 0.6 nm, about 0.1 nm to about 0.55 nm, about 0.1 nm to about 0.5 nm, about 0.1 nm to about 0.45 nm, about 0.1 nm to about 0.4 nm, about 0.1 nm to about 0.35 nm, about 0.1 nm to about 0.3 nm, about 0.1 nm to about 0.25 nm, about 0.1 nm to about 0.2 nm, about 0.1 nm to about 0.15 nm, about 0.1 nm, about 0.141 nm, about 0.15 nm, about 0.173 nm, about 0.2 nm, about 0.212 nm, about 0.25 nm, about 0.254 nm, about 0.260 nm, about 0.28665 nm, about 0.287 nm, about 0.3 nm, about 0.312 nm, about 0.35 nm, about 0.352 nm, about 0.3525 nm, about 0.35688 nm, about 0.36150 nm, about 0.362 nm, about 0.38590 nm, about 0.4 nm, about 0.40789 nm, about 0.40862 nm, about 0.424 nm, about 0.443 nm, about 0.45 nm, about 0.5 nm, about 0.52 nm, about 0.55 nm, about 0.566 nm, about 0.65 nm, about 0.693 nm, about 0.7 nm, about 0.707 nm, about 0.75 nm, about 0.8 nm, about 0.85 nm, about 0.866 nm, about 0.9 nm, or any range or value therebetween.

For FCC nanoparticles, when average lattice spacing is 0.1 nm, average lattice constants may be 0.173 nm; when average lattice spacing is 0.15 nm, average lattice constants may be 0.260 nm; when average lattice spacing is 0.18 nm, average lattice constants may be 0.312 nm; when average lattice spacing is 0.203 nm, average lattice constants may be 0.352 nm; when average lattice spacing is 0.256 nm, average lattice constants may be 0.443 nm; when average lattice spacing is 0.3 nm, average lattice constants may be 0.520 nm; when average lattice spacing is 0.4 nm, average lattice constants may be 0.693 nm; when average lattice spacing is 0.5 nm, average lattice constants may be 0.866 nm.

For BCC nanoparticles, when average lattice spacing is 0.1 nm, average lattice constants may be 0.141 nm; when average lattice spacing is 0.15 nm, average lattice constants may be 0.212 nm; when average lattice spacing is 0.18 nm, average lattice constants may be 0.254 nm; when average lattice spacing is 0.203 nm, average lattice constants may be 0.287 nm; when average lattice spacing is 0.256 nm, average lattice constants may be 0.362 nm; when average lattice spacing is 0.3 nm, average lattice constants may be 0.424 nm; when average lattice spacing is 0.4 nm, average lattice constants may be 0.566 nm; when average lattice spacing is 0.5 nm, average lattice constants may be 0.707 nm.

The present disclosure provides for a multiphasic crystalline nanoparticle selected from the group consisting of AuPdCuFeNi, CrMnFeCoNi, CrFeCoNiPd, TiNbAlCeV, and AuCuCoFe.

The present disclosure provides for a multiphasic crystalline AuPdCuFeNi nanoparticle comprising FCC and BCC phases. The present disclosure also provides for a multiphasic crystalline AuPdCuFeNi nanoparticle comprising FCC1, FCC2 and BCC phases.

The present disclosure provides for a multiphasic crystalline TiNbAlCeV ceramic nanoparticle comprising tetragonal rutile and cubic rock salt phases.

The present disclosure provides for a multiphasic crystalline TiNbAlCeVON ceramic nanoparticle comprising tetragonal rutile and cubic rock salt phases.

The present disclosure provides for a multiphasic crystalline nanoparticle for use in inhibiting bacterial growth.

The present disclosure provides for a use of a multiphasic crystalline nanoparticle in growing carbon nanotubes.

The present disclosure provides for a use of a multiphasic crystalline nanoparticle in producing hydrogen. The present disclosure provides for a use of a multiphasic crystalline nanoparticle in alkaline water electrolysis.

A facile and rapid laser annealing method to generate multicomponent metal alloy NPs of Au, Pd, Ag, Fe, Ni, Cu and Co on porous carbon nanofiber substrates and glass substrates for millisecond timescales has been described. Tuning the laser power and annealing dwell provided control to vary the multicomponent alloy (MCA)-NP size, shape, size distribution, composition and area density.

In particular, results from wide-angle X-ray scattering (WAXS), selected area electron diffraction (SAED), and atomic fraction line analysis showed that specific laser power and dwell time may promote formation of MCA NPs with new crystal structures to lower lattice strain effects via incorporation of transition metal elements.

The laser-induced restructuring of MCA NPs arises from the convergence of three process parameters: (1) annealing temperature, (2) cooling rate, (3) melt duration; and two additional intrinsic factors: (4) atomic size mismatch and (5) dissimilar electronegativities.

The laser-induced MCA-NPs showed many exciting functional properties such as catalysis for the growth of carbon nanotubes and hydrogen evolution reaction (HER) in alkaline medium as well as antibacterial effects. Finally, coupling lateral gradient laser annealing with spatial X-ray diffraction, termed as X-ray laser annealing mapping analysis (XLAM) enables high-throughput synthesis and characterization of MCA-NPs that can lead to the discovery of new nonequilibrium processing pathways towards functional high entropy alloy nanostructures and emerging applications.

List of Embodiments

1. A method of producing multiphase crystalline nanoparticle(s), comprising:
 - a. preparing a mixture of at least one metal precursor and solvent;
 - b. applying the mixture to a substrate; and
 - c. subjecting the mixture to laser irradiation for a duration of about 0.01 ms to about 500 ms, at a power of about 0.1 W to about 100 W to reach peak temperatures of 250 to 4000 °C, wherein step (c) comprises laser irradiating a mixture which does not comprise pure metal.
2. The method of embodiment 1, wherein the multiphase crystalline nanoparticle(s) comprises at least two phases and/or crystal systems selected from the group consisting of face-centred cubic (FCC), body-centred cubic (BCC), cubic rock salt, tetragonal, rutile tetragonal, hexagonal, orthorhombic, rhombohedral, monoclinic or triclinic crystal systems.
3. The method of embodiment 1 or 2, wherein the mixture comprises at least four metal precursors.
4. The method of any one of embodiments 1-3, wherein the metal precursors are selected from the group consisting of metal salts, metal oxides, metal nitrates, metal alkoxides, and combinations thereof.
5. The method of any one of embodiments 1-4, wherein the metal of the metal precursors is selected from the group consisting of Li, Be, Na, Mg, K, Ca, Rb, Sr, Ba, Fr, Ra, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Ru, Rh, Pd, Ag, Cd, W, Re, Os, Ir, Pt, Au, Hg, Nb, Ce, Al, Cs, Si, Ge, Sn, Pb and combinations thereof.
6. The method of any one of embodiments 1-5, wherein the atomic sizes of the metal of the metal precursors differ by about 5% to about 15%.
7. The method of any one of embodiments 1-6, wherein step (c) is performed with a laser having a wavelength from about 200 nm to about 700 nm, or from about 1064 nm to about 10600 nm.
8. The method of any one of embodiments 1-7, wherein step (c) is performed in an atmosphere selected from the group consisting of ambient air, unreactive gas, N₂, Ar, He, O₂, Ne, Kr, Rn, and mixtures thereof.

9. The method of any one of embodiments 1-8, wherein the substrate comprises reduced graphene oxide, graphene oxide, cellulose, chitosan, carbon, carbon nanofiber, silicon, glass, quartz, sapphire, and/or polyacrylonitrile.
10. The method of any one of embodiments 1-9, wherein the concentration of each metal precursor in the mixture of step (a) is from about 0.01 M to about 10 M.
11. The method of any one of embodiments 1-10, wherein the solvent is selected from the group consisting of water, alcohols, ketones, ethers, amides, lactones, lactams, sulfones, sulfoxides, alkanes, alkenes, and combinations thereof.
12. The method of any one of embodiments 1-11, wherein step (b) comprises dropcasting the mixture onto the substrate or immersing the substrate in the mixture.
13. The method of any one of embodiments 1-12, wherein the method produces multiphasic crystalline nanoparticle(s) of AuPdCuFeNi, CrMnFeCoNi, CrFeCoNiPd, TiNbAlCeV, TiNbAlCeVO, TiNbAlCeVON, TiNbAlCeVN, AuCuCoFe, AgCu or AuCuFe.
14. The method of any one of embodiments 1-13, wherein the method comprises:
 - a. preparing a mixture of at least two metal precursors selected from the group consisting of salts, oxides, nitrates and/or alkoxides of Au, Pd, Cu, Fe, Ni, Ti, Nb, Al, Ce, V, Cr, Mn, Co, Cs, Si, Ge, Sn, and Pb;
 - b. applying the mixture to a substrate; and
 - c. subjecting the mixture to laser irradiation for a duration of about 0.25 ms to about 500 ms, at a power of about 0.5 W to about 12 W to reach peak temperatures of about 1000 °C to about 4000 °C,
 wherein step (c) comprises laser irradiating a mixture which does not comprise pure metal.
15. A multiphasic crystalline nanoparticle produced by the method of any one of embodiments 1-14.
16. A multiphasic crystalline nanoparticle comprising at least four metals selected from the group consisting of Li, Be, Na, Mg, K, Ca, Rb, Sr, Ba, Fr, Ra, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Ru, Rh, Pd, Ag, Cd, W, Re, Os, Ir, Pt, Au, Hg, Nb, Ce, Al, Cs, Si, Ge, Sn, Pb and combinations thereof, and at least two phases/and or crystal structures selected from the group consisting of FCC, BCC, cubic rock salt, tetragonal, rutile tetragonal, hexagonal, orthorhombic, rhombohedral, monoclinic or triclinic crystal systems.
17. The nanoparticle of embodiment 16, wherein the nanoparticle has an average particle diameter from about 3 nm to about 500 nm.
18. The nanoparticle of embodiment 16 or 17, wherein the nanoparticle has an average lattice spacing from about 0.1 nm to about 0.5 nm.
19. The nanoparticle of any one of embodiments 16-18, wherein the nanoparticle has an average lattice constant from about 0.1 nm to about 0.9 nm.
20. The nanoparticle of any one of embodiments 16-19, wherein the nanoparticle is selected from the group consisting of AuPdCuFeNi, CrMnFeCoNi, CrFeCoNiPd, TiNbAlCeV, TiNbAlCeVO, TiNbAlCeVON, TiNbAlCeVN, and AuCuCoFe.
21. The nanoparticle of any one of embodiments 16-20, wherein the nanoparticle is AuPdCuFeNi and comprises FCC and BCC phases.
22. The nanoparticle of any one of embodiments 16-20, comprising five metals selected from Ti, Nb, Al, Ce and V, and at least a cubic rock salt phase and at least a rutile tetragonal crystal system.

23. A multiphasic crystalline nanoparticle of any one of embodiments 15 to 21, for use in inhibiting bacterial growth.

Examples

Non-limiting examples of the invention and comparative examples will be further described in greater detail by reference to specific examples, which should not be construed as in any way limiting the scope of the invention.

Example 1: Synthesis of substrate

Example 1a: Synthesis of carbon nanofiber (CNF) substrate

Polyacrylonitrile (PAN) was dissolved in dimethylformamide (DMF) solvent (8 % w/w) under vigorous stirring for 4 hours. 3 mL of the PAN solution was loaded into an electrospinner instrument (MECC Co. Ltd. Nanon-01B) and run at a rotation speed of 50 revolutions per minute (rpm), excitation voltage of 15 kV, spinning distance of 10 cm, and feed rate of 1 mL/h to form the PAN nanofiber substrate. The PAN nanofiber substrate was collected on a piece of aluminum foil and stabilized at 260 °C under ambient environment for 5 hours, followed by carbonization under N₂ at 800 °C at 2 hours with a ramping rate of 5 °C/min to yield the CNF substrate. The porous CNF substrate was secured on a silicon substrate with 3M adhesive tape for laser heating experiment.

Example 1b: Synthesis of graphene oxide (GO)/glass substrate

1 g of phosphorus pentoxide (P₂O₅) and 3 g of potassium permanganate (KMnO₄) was added to 23 ml of concentrated sulfuric acid (H₂SO₄, 98%) with stirring for 3 minutes in ice. 0.5 g of sodium nitrate (NaNO₃) and 0.5 g of graphene nanopowder was premixed by grinding. The obtained powder was added into the mixture and stirred at 0 °C for 10 minutes, and then slowly warmed up to 35 °C and stirred for another 1 hour. 10 ml of deionized (DI) water was added dropwise slowly into the mixture, followed by increasing the temperature of the mixture to 85 °C for 15 minutes before cooling to room temperature. 10 ml of hydrogen peroxide solution (H₂O₂, 30%) was added dropwise to form a bright yellow coloration that indicated the presence of highly oxidized GO. The contents of the flask were washed with 1 M HCl thrice and twice thereafter with DI water. The resulting GO dispersion was dialyzed in DI water with a 12.4 kDa cellulose membrane dialysis tubing for 3–4 days and the dialyzing solution was changed once every 12 hours. The resultant mixture was centrifuged at 8500 rpm for 5 minutes and redispersed in DI water for storage. A few droplets of GO dispersion in DI water were drop-casted on the borosilicate glass capillary tube to form the GO/glass substrate.

Example 2: Preparation of metal precursor mixtures on substrate

Metal precursor mixtures affixed on substrates were prepared to synthesise the nanoparticles using laser irradiation. Briefly, 0.5 mmol of each individual metal precursor was dissolved in separate vials using 10 mL of solvent to form 0.05 M precursor solutions. 1 mL aliquots of each metal precursor solution were then mixed to obtain the precursor solution having a total precursor concentration of 0.05 M. 0.36 mL of the final metal precursor solution was used and drop-casted on a substrate to form the mixture for subsequent laser annealing.

Example 2a-i: AuPdCuFeNi on CNF

88.6 mg (0.5 mmol) PdCl₂, 196.9 mg (0.5 mmol) HAuCl₄·3H₂O, 112.7 mg (0.5 mmol) CuCl₂·5H₂O, 88.1 mg (0.5 mmol) FeCl₃ and 94.5 mg (0.5 mmol) NiCl₂·3H₂O were dissolved in separate vials, each containing 10 mL of ethanol as solvent. 1 mL aliquots of the individual metal precursor solutions were mixed to obtain a quinary metal precursor solution (total metal precursor concentration of 0.05M and total volume of 5 mL). 0.36 mL of the quinary metal precursor solution was then drop-casted

on a CNF substrate of Example 1a (about 10 mm × 30 mm × 0.06 mm). The precursor mixture on substrate was dried under ambient conditions.

Example 2a-ii: AuPdCuFeNi on GO/glass

Example 2a-ii was prepared in the same way as Example 2a-i, except that 0.36 ml of precursor solution was drop-casted on the GO/glass substrate of Example 1b. The precursor mixture on substrate was dried under ambient conditions.

Example 2b: TiNbAlCeV

38.1 mg (0.5 mmol) $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 38.1 mg (0.5 mmol) $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.03 ml (0.5 mmol) $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, 0.03 ml (0.5 mmol) $\text{Nb}(\text{OCH}_2\text{CH}_3)_5$, and 0.03 ml (0.5 mmol) $\text{VO}(\text{OCH}(\text{CH}_3)_2)_3$ were dissolved in separate vials, each containing 10 mL of ethanol as solvent. 1 mL aliquots of the individual metal precursor solutions were mixed to obtain a quinary metal precursor solution (total metal precursor concentration of 0.05M and total volume of 5 mL). 0.36 mL of the quinary metal precursor solution was then drop-casted on a CNF substrate of Example 1a (about 10 mm × 30 mm × 0.06 mm). The CNF substrate coated with the precursor mixture was dried under ambient conditions.

Example 2c: CrMnFeCoNi

200.01 mg (0.5 mmol) $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 125.5mg (0.5 mmol) $\text{Mn}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, 119.0 mg (0.5 mmol) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 88.1 mg (0.5 mmol) FeCl_3 and 94.5 mg (0.5 mmol) $\text{NiCl}_2 \cdot 3\text{H}_2\text{O}$ were dissolved in separate vials with 10 mL of ethanol as solvent. 1 mL aliquots of the respective salt solutions were mixed to obtain the quinary salt precursor solution (total metal precursor concentration of 0.05M and total volume of 5 mL). 0.36 mL of the quinary CrMnFeCoNi precursor solution was drop-casted on the CNF scaffold of Example 1a (~10 mm × 30 mm × 0.06 mm) for coating. The CNF substrate coated with the precursor mixture was dried under ambient conditions.

Example 2d: CrFeCoNiPd

200.01 mg (0.5 mmol) $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 119.0 mg (0.5 mmol) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 88.1 mg (0.5 mmol) FeCl_3 , 94.5 mg (0.5 mmol) $\text{NiCl}_2 \cdot 3\text{H}_2\text{O}$, and 88.6 mg (0.5 mmol) PdCl_2 were dissolved in separate vials with 10 mL of ethanol as solvent. 1 mL aliquots of the respective salt solutions were mixed to obtain the quinary salt precursor solution (total metal precursor concentration of 0.05M and total volume of 5 mL). 0.36 mL of the quinary CrFeCoNiPd precursor solution was drop-casted on the CNF scaffold of Example 1a (~10 mm × 30 mm × 0.06 mm) for coating. The CNF substrate coated with the precursor mixture was dried under ambient conditions.

Example 2e: AuCuCoFe

196.9 mg (0.5 mmol) $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 112.7 mg (0.5 mmol) $\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$, 119.0 mg (0.5 mmol) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and 88.1 mg (0.5 mmol) FeCl_3 were dissolved in separate vials with 10 mL of ethanol as solvent. 1 mL aliquots of the respective salt solutions were mixed together to obtain the quaternary salt precursor solution (total metal precursor concentration of 0.05 M and total volume of 4 mL). 0.36 mL of the quaternary AuCuCoFe precursor solution was drop-casted on the CNF scaffold of Example 1a (~10 mm × 30 mm × 0.06 mm) for coating. The CNF substrate coated with the precursor mixture was dried under ambient conditions.

Example 2f: AgCuFe

84.94 mg (0.5 mmol) AgNO_3 , 93.8 mg (0.5 mmol) $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and 88.1 mg (0.5 mmol) FeCl_3 were dissolved in separate vials with 10 mL of ethanol as solvent. 1 mL aliquots of the respective salt solutions were mixed together to obtain the ternary salt precursor solution (total metal precursor concentration of 0.05 M and total volume of 3 mL). 0.36 mL of the ternary AgCuFe precursor solution

was drop-casted on the CNF scaffold of Example 1a (~10 mm × 30 mm × 0.06 mm) for coating. The CNF substrate coated with the precursor mixture was dried under ambient conditions.

Example 2g: AgCu

84.94 mg (0.5 mmol) AgNO₃ and 93.8 mg (0.5 mmol) Cu(NO₃)₂·3H₂O were dissolved in separate vials with 10 mL of ethanol as solvent. 1 mL aliquots of the respective salt solutions were mixed together to obtain the binary salt precursor solution (total metal precursor concentration of 0.05 M and total volume of 2 mL). 0.36 mL of the binary AgCu precursor solution was drop-casted on the CNF scaffold of Example 1a (~10 mm × 30 mm × 0.06 mm) for coating. The CNF substrate coated with the precursor mixture was dried under ambient conditions.

Example 2h: Pd

88.6 mg (0.5 mmol) PdCl₂ was dissolved in a vial with 10 mL of ethanol as solvent. 0.36 mL of the Pd precursor solution was drop-casted on the CNF scaffold of Example 1a (~10 mm × 30 mm × 0.06 mm) for coating. The CNF substrate coated with the precursor mixture was dried under ambient conditions.

Example 2i: Ti

0.03 ml (0.5 mmol) Ti(OCH(CH₃)₂)₄ was dissolved in a vial with 10 mL of ethanol as solvent. 0.36 mL of the precursor solution was then drop-casted on a CNF substrate of Example 1a (about 10 mm × 30 mm × 0.06 mm). The CNF substrate coated with the precursor mixture was dried under ambient conditions.

Example 3: Laser annealing of metal precursor samples

Briefly, a continuous wave 532 nm semiconductor laser was focused to a line beam profile with a full-width-half-maximum (FWHM) of approximately 0.1 mm by 0.4 mm. The visible laser line beam was scanned across the samples of Example 2 via dynamic sample stage motion at velocities of 0.4 mm/s to 400 mm/s, resulting in 0.4 μm wide FWHM scan lines for dwell times of 0.25 ms to 250 ms. The samples of Example 2 were irradiated either under nitrogen in a custom-built chamber with a quartz window or in ambient air.

For larger scanned areas, the samples were instead irradiated with a single overlapping pass using a 0.01 mm step size. After irradiation, any remaining precursors in non-irradiated regions were removed by rinsing in warm water.

Multicomponent NPs were generated based on the laser-induced melt-mediated crystallization process. After irradiation, the precursors melted and carbothermally reduced into globular liquid droplets to minimize surface energy on the non-wetting CNF surface, with the concurrent release of gaseous byproducts. Cooling due to thermal conduction into the substrate induced solidification of liquid droplets into crystalline multicomponent inorganic NPs.

The respective absorption coefficients of each metal at the wavelength of 532 nm are shown in Fig. 1.

Lateral gradient laser scanning and spatial X-ray diffraction

X-ray laser annealing mapping analysis (XLAM) enables high-throughput exploration of the correlation between annealing parameters and the corresponding NP structure correlations by combining lateral gradient laser scanning with spatial X-ray diffraction. In this present invention, XLAM has been used to study the nanoparticle phases and/or crystal systems under different laser annealing conditions in a single run to establish the process-structure correlations.

In the lateral direction, the laser beam has a Gaussian intensity profile that provides a spatial distribution of laser powers – maximum power and peak temperature at the beam center and decreasing toward either edge. Figs. 23a and 23b show the 1-D intensity profile plots of a line-focused Gaussian laser beam with FWHM values of about 0.1 mm by 0.4 mm. Laser scanning of the sample thus results in a line of spatially annealed high entropy alloy nanoparticles (HEA-NPs) where powers and temperatures are uniform along the scan length but vary across the scan width. As such, within a single scan line, the sample is locally laser-annealed at different power levels and temperatures for the same heating dwell.

An incident X-ray beam was then scanned across this profile in the sample in the direction orthogonal to the laser scan width and the diffracted signals collected by the detector. Discrete WAXS data of HEA-NPs within a single laser-annealed scan line were mapped as a function of the spatial positions (laser powers and temperatures) for the same annealing dwell.

Example 4: Characterizing the nanoparticles

Scanning electron microscopy (SEM) was performed using a JEOL 7600F field emission scanning electron microscope equipped with a half-in-lens detector. Transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS) were conducted with a JEOL 2100F electron microscope, equipped with the Gatan Ultrascan 1000XP CCD camera, Gatan Digiscan and STEM detectors as well as an EDAX EDS detector, operating at an accelerating voltage of 200 kV. EDS spectrums were collected with a windowless 100 mm² Oxford Ultim Max Silicon Drift Detector. Selective area electron diffraction patterns were analyzed using a Gatan DigitalMicrograph 3.5 software.

WAXS and spatial X-ray laser annealing mapping (XLAM) measurements were performed with a Xenocs Nano-inXider in the transmission mode using a Cu K_α radiation source and Dectris Pilatus 3 detectors. The WAXS measurements were smoothed with a FFT filter operation in the GenPlot software. UV-vis measurements were conducted using a Cary 5000 UV-Vis NIR spectrophotometer. X-ray photoelectron spectroscopy (XPS) analysis was performed using an AXIS Supra spectrometer (Kratos Analytical, UK) equipped with a hemispherical analyzer and a monochromatic Al K_α source (1487 eV) operating at 15 mA and 15 kV. The XPS spectra were acquired from an analysis area of 700 × 300 μm² at a take-off angle of 90°. A pass energy of 160 eV and 20 eV was used for survey and high-resolution scans respectively. A 3.1 V bias was applied to prevent charge build-up on the sample. The samples were prepared by pressing the high entropy ceramic-nanoparticles-carbon nanofiber (HEC-NP-CNF) film samples on carbon tape. Due to the propensity of nitride materials oxidizing in ambient air, the HEC-NP-CNF samples were sputter-cleaned with the gas cluster ion source (10 keV, Ar1000+) for 5 minutes to remove surface oxidation.

Example 4a: Characterizing mono-Pd nanoparticles

Fig. 37 and 40 show a series of SEM images of mono-Pd NPs formed with different shapes, sizes and size distributions, produced after laser annealing the precursor mixture of Example 2h under various laser powers and heating dwells. Fig. 5b shows the HAADF-STEM image and EDS image of Pd-NPs generated by laser irradiation at 2 W for 0.25 ms.

Figs. 42a-b show SEM images of the uncoated CNF substrate, while Figs. 42c-d show SEM images of PdCl₂-coated CNF substrates prior to laser annealing for comparison. Fig. 42e shows the diameter measurements of both the uncoated and PdCl₂-coated CNF substrates of Figs. 42a-b and Figs. 42c-d respectively. From the graph, it was calculated that the PdCl₂ precursor was coated with an average thickness of about 40 nm around the CNF substrate.

Laser Powers

Fig. 37 shows spherical mono-Pd NPs uniformly dispersed on the CNF substrate surface after laser annealing at 2 W for 0.25 ms, with a mean diameter of ~ 5.3 nm and having a narrow size distribution (see (a) of Fig. 37, and curve denoted by squares in Fig. 38a). The high-resolution transmission electron micrograph (HR-TEM) image in Fig. 38b shows the crystalline fringes of the mono-Pd NP with an average lattice spacing of 0.220 nm, which is consistent with the (111) plane of FCC Pd.

For the same annealing dwell of 0.25 ms, while the NP size and size distribution remained relatively unchanged after irradiation at 4 W (see (e) of Fig. 37), the mean diameter increased to ~ 13.8 nm along with a wider size distribution and a lower area density on the CNF substrate surface after laser annealing at 6 W (see (i) of Fig. 37i).

Hence it can be seen that an increase in laser power results in an increase in nanoparticle diameter size. The size distribution of the nanoparticles also increases at higher laser powers, but the area density of the NPs on the substrate are lowered at increasing laser powers.

Dwell Times

Similar observations were made for longer annealing dwells. Fig. 37 showed that the diameter of the mono-Pd NPs successively increased from ~ 5.3 nm to 20.7, 42.4 and 99.1 nm when dwell times were increased from 0.25 ms to 0.75 ms, 2.5 ms and 7.5 ms respectively, while maintaining a laser power of 2 W (see (a) to (d) of Fig. 37).

The size distribution of the mono-Pd NPs, similarly, gradually widened with increasing dwell times at higher laser powers of 4 W (see (e) to (h) of Fig. 37) and 6 W (see (i) to (l) of Fig. 37).

Hence, it can be seen that the size of the NPs increases with increasing dwell times.

A formation mechanism combining the concepts of laser-induced melt-crystallization and characteristic time analyses of nanocluster growth is accordingly proposed here.

Upon laser irradiation, photons are absorbed by the PdCl_2 coating the CNF substrate and converted into thermal energy. The PdCl_2 is brought above the melting point ($T \geq 952$ K) by the photothermal process and is then melted into liquid Pd and gaseous by-products.

For laser annealing at low powers and sub-millisecond dwells, liquid Pd redisperses and nucleates into spherical droplets to minimize the surface energy on the CNF surface, followed by solidification into crystalline mono-Pd NPs. A graph showing the melting point of Pd versus particle diameter is shown in Fig. 39a. The formation of spherical NPs at short dwells (≤ 7.5 ms) is likely due to the rapid laser-induced heating and quenching phenomena, resulting in kinetically trapped Pd NPs with crystalline facets of very similar surface energies and thereby evenly rounded shape (Fig. 37).

Characteristics time analyses of annealing dwells between 0.25 ms to 7.5 ms suggest that the growth of mono-Pd NPs was dominated by Brownian coagulation and Ostwald ripening mechanisms (see shaded region in Fig. 39b). It is posited that Brownian coagulation had the shortest characteristic time (see dashed line in Fig. 39b) as the less-than-favorable interactions of liquid Pd with the carbon surface imparted high mobility to the Pd nanoclusters, thereby inducing random collision and binding of nanoclusters. As the mono-Pd NPs became larger and less mobile, the characteristic time of Brownian coagulation increased (10^{-6} s for <100 nm particles) but was still shorter than sub-millisecond dwell time of the laser annealing process. Contrarywise, the kinetics of Ostwald ripening (see dashed-dotted line in Fig. 39b) which involved dissolution of smaller nanoclusters followed by the re-deposition of Pd atoms on larger NPs reached a steady state as the NPs grew to sizes of ~ 50 nm ($\sim 10^{-3}$ s).

Laser Powers beyond 6 W

Laser annealing at even higher powers and longer dwells produced mono-Pd NPs with larger shape and size diversities, broader size distributions as well as smaller area densities. For instance, Fig. 40 showed that annealing at 10 W to 14 W for dwells of 1 ms to 7.5 ms resulted in various forms of NP aggregations, Pd-catalyzed carbon nanotube growth (Figs. 40g, i and j) and ablation of CNF substrate (Figs. 40h, k and l, respectively).

It is hypothesised that higher laser powers and longer dwells may have increased the melt durations, enabling liquid Pd atoms to organize into (111) crystal facets and form a distinctive truncated shape to lower the surface energy (Fig. 40b-c). However, aggregations of the NPs were also observed, likely as a result of the larger-sized NPs having lower mobilities and thus remained kinetically trapped in less stable irregular shapes (Fig. 40d). Moreover, the CNF substrate became increasing graphitized, which corresponded to lower concentration of defects on the CNF surface, thereby impeding NP mobility and size uniformities (see Fig. 41).

It is worth mentioning that control experiments showed that mono-Pd NPs were also generated by laser annealing in ambient air at 10 W power for 0.25 ms (Figs. 25a-b). However, the resultant NPs became transient hotspots after irradiation and induced localized oxidation and formation of potholes on the CNF surface.

Example 4b: Characterizing AuPdFeCuNi HEA-NPs

Fig. 2 shows a SEM image of AuPdFeCuNi HEA-NPs formed after the substrate of Example 2a-ii was laser annealed at 2 W for 0.25 ms. The NPs were observed with an average diameter of 13.8 ± 1.2 nm. The HR-TEM image of the AuPdFeCuNi HEA-NP as shown in Fig. 3 revealed a spherical NP with a broad lattice spacing distribution from 0.203 nm to 0.256 nm, consistent with the lattice spacing values of the pure constituent metals (see Table 1).

This was corroborated by WAXS data shown in Fig. 4 (see 2 W curve) displaying broad (111) and (200) reflections at 2θ values of 38.6° and 44.6° consistent with the face-centered cubic (FCC) ($a_{\text{FCC}}=0.403$ nm), as well as a weaker reflection at $2\theta = 41.8^\circ$, suggestive of a secondary alloy phase.

Table 1. Physical properties of metal precursors and pure metals.

Sample	Atomic Radius (pm)	Melting Point (°C)	χ (Pauling Scale)	Crystal Structure (at 300 K)	Lattice spacing (nm)	Lattice constant (nm)	Standard Reduction Potential (eV)
HAuCl ₄		254		Monoclinic			
PdCl ₂		679		Rhombohedral			
CuCl ₂		100		Distorted			
NiCl ₂		1001		Monoclinic			
FeCl ₃		306		Hexagonal			
AgNO ₃		212		Orthorhombic			
CoCl ₂		737		Octahedral			
Au	144	1064	2.4	FCC	$d_{111} = 0.2355$ (PDF 01-071-4073)	0.40789	1.52 (Au ³⁺ /Au)
Pd	137	1555	2.2	FCC	$d_{111} = 0.22280$ (PDF 04-015-9347)	0.38590	0.915 (Pd ²⁺ /Pd)
Cu	128	1085	1.9	FCC	$d_{111} = 0.20880$ (PDF 00-004-0836)	0.36150	0.3419 (Cu ²⁺ /Cu)
Ni	125	1455	1.8	FCC	$d_{111} = 0.20352$ (PDF 01-070-1849)	0.35250	-0.257 (Ni ²⁺ /Ni)

Fe	124	1538	1.8	BCC	$d_{110} = 0.20269$ (PDF 01-071-3763)	0.28665	-0.037 (Fe ³⁺ /Fe)
Ag	144	962	1.9	FCC	$d_{111} = 0.23590$ (PDF 00-004-0783)	0.40862	0.7996 (Ag ⁺ /Ag)
Co	125	1495	1.8	HCP	$d_{111} = 0.20604$ (PDF 01-071-4238)	0.35688	-0.277 (Co ²⁺ /Co)

High-angle annular dark field scanning transmission electro micrograph (HAADF-STEM) and EDS mapping analysis in Fig. 5a indicated that the elemental distributions in the AuPdFeCuNi NPs were macroscopically homogeneous with only limited aggregation. Closer examination of the EDS atomic fraction line profiles in Fig. 6a revealed fluctuations of Au and Pd suggesting an Au-core surrounded by a Pd-rich shell. In particular, Au had a maximum atomic fraction of ~76% in the center which was reduced to 25% at the edge of the nanoparticle. Pd exhibited the largest segregation with 20% concentration in the center and 84% at the edge. The lighter transition metals Cu, Fe and Ni had smaller mean atomic fractions of 11%, 4% and 2%, respectively. The results are summarized in Table 2.

Table 2. Nominal compositional distributions of laser-annealed AuPdFeCuNi HEA-NPs obtained from EDS measurements.

Laser Power (W)	Heating Dwell (ms)	Atomic Fraction				
		Au	Pd	Cu	Ni	Fe
2	0.25	0.469	0.351	0.112	0.025	0.043
2	2.5	0.321	0.356	0.047	0.107	0.169
2	25	0.440	0.123	0.237	0.074	0.126
2	250	0.363	0.266	0.108	0.094	0.169
0.6	2.5	0.638	0.250	0.044	0.011	0.057

The local compositional inhomogeneities in the HEA-NPs were induced by the presence of larger and more electronegative Au and Pd atoms relative to the smaller electropositive Cu, Ni and Fe atoms. As Au(III) has the highest reduction potential, it likely nucleated first followed by other metal cations, forming the Au@PdCuFeNi core-shell heterostructure. Moreover, the metal atomic fractions were observed to correlate with the respective reduction potentials, suggesting the HEA-NP formation is thermodynamically favorable despite the short heating time.

Dwell time

From finite element analysis (FEA) as described in Example 5, it was observed that the peak annealing temperatures increased with laser powers and dwells, and that melt can persist for an order of magnitude longer than the heating dwell. Upon irradiation at 2 W for 0.25 ms, the precursor salt mixture melted and carbothermally reduced into globular liquid metal droplets to minimize surface energy on the non-wetting CNF surface. It was noted that the corresponding temperature, cooling rate and melt duration were 1830 °C, 10⁵ K/s and 2.5 ms respectively. Although liquid metal atoms are highly mobile ($\sqrt{D_s \tau} \approx 10^{-6}$ m; see Fig. 32 and Table 4), it is likely large-scale migration does not occur during initial homogenization due to the short melt duration and high temperature quench rate, resulting in liquid phase segregation and subsequent solidification into sub-20-nm spherical core-shell structured HEA NPs with similar surface energy facets (see Fig. 3).

Increasing laser annealing dwells of the same metal precursor mixture led to higher peak temperatures, longer melt durations and slower cooling rates. The same irradiation at 2 W for 2.5 ms increased the peak temperature to ~3165 °C and was accompanied by a slower cooling rate of about 10⁴ K/s and a longer melt time of about 33 ms, which enabled the liquid metal droplets to grow into larger NPs (53 ± 9 nm) through coarsening. It was further observed that the liquid metal atoms, especially Fe and Ni, were able to diffuse further ($\sqrt{D_s \tau} \approx 10^{-5}$ m) (Fig. 32, Tables 3 and 4) promoting

more homogeneous intermixing of atoms and solidifying into energetically favorable FCC $\langle 111 \rangle$ crystal facets to yield the truncated NP shape (Fig. 7a). However, the increased presence of transition metal stabilizers (Ni for FCC1/2 and Fe for BCC) and a lower strain energy penalty may encourage the formation of less densely packed BCC phase to relieve the overall lattice distortion associated with the large atomic size differences (Figs. 6b, 11, and Table 2). This allowed for the tailoring of HEA-NP size, size distribution, shape, and most importantly, atomic composition and crystal structure.

Table 3. Surface diffusivity D_s values of pure metals at peak laser annealing temperatures for various dwells obtained from Fig. 32

Annealing Dwell (ms)	T_{peak} (°C)	Surface Diffusivity, D_s (cm ² /s)				
		Au	Pd	Cu	Ni	Fe
0.25	1830	2.2×10^{-4}	4.8×10^{-5}	2.1×10^{-4}	6.5×10^{-5}	5.0×10^{-5}
2.5	3165	1.1×10^{-3}	4.3×10^{-4}	1.1×10^{-3}	5.2×10^{-4}	4.5×10^{-4}
25	3580	1.5×10^{-3}	6.3×10^{-4}	1.4×10^{-3}	7.5×10^{-4}	6.5×10^{-4}
250	3590	1.5×10^{-3}	6.3×10^{-4}	1.4×10^{-3}	7.5×10^{-4}	6.5×10^{-4}

Table 4. Characteristic diffusion distance values of pure metals at peak laser annealing temperatures for different dwells

Annealing Dwell (τ , ms)	T_{peak} (°C)	Diffusion Distance, $\sqrt{D_s \tau}$ (m)				
		Au	Pd	Cu	Ni	Fe
0.25	1830	2.3×10^{-6}	1.1×10^{-6}	2.3×10^{-6}	1.3×10^{-6}	1.1×10^{-6}
2.5	3165	1.7×10^{-5}	1.0×10^{-5}	1.7×10^{-5}	1.1×10^{-5}	1.1×10^{-5}
25	3580	6.1×10^{-5}	4.0×10^{-5}	5.9×10^{-5}	4.3×10^{-5}	4.0×10^{-5}
250	3590	1.9×10^{-4}	1.3×10^{-4}	1.9×10^{-4}	1.4×10^{-4}	1.3×10^{-4}

SEM (Fig. 7a and Fig. 8a) and HAADF-STEM (Fig. 9a) images showed that the AuPdCuFeNi NPs were formed with a faceted truncated shape and a diameter of ~30 to 60 nm when exposed to laser annealing at 2 W for 2.5 ms dwell (~3165 °C), as compared to a dwell time of 0.25 ms.

From the WAXS data in Fig. 10, multiple intense peaks were observed for the 2.5 ms dwell, indicating the NPs contained multiple crystalline phases. The second primary peak at the angular position of $1/d = 4.52 \text{ nm}^{-1}$ could be indexed to either a second FCC (FCC2) or a body-centered cubic (BCC) structure.

SAED with a larger angular range was performed to corroborate the WAXS data. SAED patterns in Figs. 11-13 exhibited three characteristic sets of diffraction spots consistent with dual FCC phases (FCC1/2) and another BCC lattice (Table 5). From the 1D SAED integrated intensity curve (Fig. 11), multiple reflections near 6.4 and 9.9 nm^{-1} were observed, consistent with BCC (200) and (310) planes respectively. The EDS atomic fraction line profiles in Fig. 6b indicated the quinary HEA-NPs after 2.5 ms dwell were macroscopically homogeneous with increased amounts of Fe and Ni at 11% and 17% respectively.

Table 5. Selected Area Electron Diffraction (SAED) analysis of laser-induced AuPdFeCuNi HEA NPs after laser annealing at 2 W for 2.5 ms

Phase	Plane	Expected Angular Positions ($1/d$, nm ⁻¹)	Measured Angular Positions ($1/d$, nm ⁻¹)		
			Pattern No. 1	Pattern No. 2	Pattern No. 3
fcc1	111	4.24	4.28	4.29	4.38
	200	4.9	4.83	4.84	4.83
	220	6.93	6.97	6.95	7.06
	311	8.13			
	222	8.49	8.4	8.48	8.51
	400	9.8		9.79	
bcc	110	4.51	4.59	4.61	4.64
	200	6.38	6.06	6.51	6.17
	211	7.82	7.85	7.82	
	220	9.03	8.8	8.87	8.91
	310	10.09	10.08	10.15	
	222	11.06	11.02	11.16	11.06
fcc2	111	4.51	4.59	4.61	4.64
	200	5.21	5.06	5.21	5.21
	220	7.37	7.41	7.23	
	311	8.64			
	222	9.03			
	400	10.42	10.37		10.43
	311	11.36	11.44	11.36	

Comparatively, HEA-NPs grew to 109 ± 29 nm and 228 ± 32 nm at longer dwells of 25 ms (~ 3580 °C, see Figs. 7b, 8b and 9b) and 250 ms (~ 3590 °C, see Figs. 7c, 8c and 9c) respectively, while their NP shape evolved from having faceted features to having more rounded corners.

The strongly scattering WAXS patterns in Fig. 10 (see 2.5ms, 25 ms and 250 ms curves) indicated the dominant phase was FCC2 ($a_{\text{FCC2}} = 0.382$ nm), while EDS atomic line profiles in Figs. 6b–6d suggested increased amounts of Cu and Ni were responsible as FCC stabilizers (see Figs. 9a–9c and Table 2). Preservation of the truncated NP shape at 25 ms dwell (see Fig. 7b) suggested that the liquid remained sufficiently agile to form thermodynamically stable FCC2 $\langle 111 \rangle$ surfaces under similar cooling rates ($\sim 10^4$ K/s). For 250 ms dwell however, the slower cooling rate ($\sim 10^3$ K/s) provided lower thermocapillary driving force and impeded atomic diffusion kinetics for shape regulation of larger NPs despite longer melt times. It was further observed that the latent heat released by the HEA-NPs during the solidification process would extend the duration of the melt state. Upon cooling, the newly formed HEA-NPs were instead smaller in size and widened the overall NP dispersity as a result (Fig. 8b-c).

Thus, it is hypothesized that the laser-induced restructuring of HEA-NPs arises from the convergence of three process parameters: (1) annealing temperature, (2) cooling rate, (3) melt duration; and two additional intrinsic factors: (4) atomic size mismatch and (5) dissimilar electronegativities.

Laser Powers

XLAM, as described earlier in Example 3, was used to study the correlation between laser power and the AuPdFeCuNi HEA-NP characteristics.

Briefly, AuPdFeCuNi HEA-NPs were formed after irradiation at 6 W for 0.25 ms. Figs. 21a and 21b display the representative 2D XLAM profile of said AuPdFeCuNi HEA-NPs and corresponding integrated intensity plots. Fig. 23c indicated the crystalline samples across the laser scan width (from scan center) were equivalent to samples irradiated individually at 3 W and 4 W.

At the center of the laser scan line ($s_{xy} = 0$ mm), the dominant phase was FCC2 phase as indicated by the strong intense reflection at $2\theta = 41.6^\circ$. Across the laser scan width, the primary WAXS peaks broadened and shifted to smaller angular position range of 40° – 41° , indicating formation of multiphasic HEA-NPs with larger lattice constants at lower powers and increased FCC1 phase stability (Fig. 23c and 4).

Example 4c: Characterizing TiNbAlCeV-based HEC-NPs

The laser annealing process of Example 3 was extended to produce HEC-NPs using a combination of nitride-forming elements, in particular, Ti, Nb, Al, Ce, and V. From the SEM images of Fig. 14, the diameters of laser-induced HEC-NPs ranged from 28 ± 7 nm (2 W), 62 ± 12 nm (6 W) to 167 ± 69 nm (12 W).

In the WAXS spectrum (Fig. 15) at a laser power of 2 W, several distinct reflections consistent with the tetragonal rutile structure and typical of the constituent metal oxides (e.g., rutile phase of TiO_2 , NbO_2 , VO_2) were observed. XPS peak-differentiation-imitating analysis of the 2 W sample indicated a majority of the component peaks corresponded to the metal oxides (denoted as TiNbAlCeVO_x). The formation of TiNbAlCeVO_x tetragonal rutile oxide NPs (space group $P4_2/mnm$) after millisecond laser annealing at 2 W, in contrast to AuPdFeCuNi NPs, could be attributed to the presence of alkoxides of Ti, V and Nb in the precursor mixture. Fig. 14a shows the SEM images of the same HEC-NPs.

Laser Power

When laser powers were increased to 4 and 6 W, the reflections in the WAXS spectrum (Fig. 15) of the crystalline TiNbAlCeV -based NPs first gained intensity (4 W), and then slightly diminished with the appearance of a new set of reflections (6 W), suggesting an impending crystalline phase transition from the tetragonal rutile structure. The new reflections positioned at angular positions of 35.6° , 41.6° and 60.4° at 10 W to 12 W were consistent with the cubic rock salt structure (space group $Fm\bar{3}m$). The cubic rock salt structure became the dominant phase in the samples of increasingly higher laser powers up to 12 W. Trace oxygen likely remained even after annealing at 12 W, as indicated by the minor peaks between 25° and 30° .

HAADF-STEM EDS mapping analysis of the laser-annealed TiNbAlCeV -based NP samples at 12 W (Fig. 16) indicated all five metal species were homogeneously distributed in the particle along with nitrogen and some oxygen, indicating the prevalent phase was the oxynitride cubic rock salt structure.

High resolution XPS was also employed to characterize the valence states and compositions of the metallic constituents in the TiNbAlCeV -based samples after laser irradiation at 2, 6 and 12 W, respectively. The XPS spectra in Figs. 17a-c and 18a-b exhibited the core level peaks of Ti $2p$, Nb $3d$, Al $2p$, Ce $3d$ and V $2p$ for all laser-annealed TiNbAlCeV -based samples (Table 6). Figs. 14b and 14c show the representative SEM images of the HEC-NPS annealed on CNF scaffold at 6 W and 12 W for 0.25 ms respectively.

Table 6. Binding energy (BE) values of respective component peaks and atomic concentrations in the TiNbAlCeV -based samples after laser irradiation at 2, 6 and 12 W, respectively, all for 0.25 ms.

Sample	State	BE (eV)	Assignment	at. %	State	BE (eV)	Assignment
2 W	Ti $2p_{3/2}$	458.61	Ti(IV)–O	70.88	Nb $3d_{5/2}$	207.13	Nb(V)–O
		456.87	Ti(III)–O	24.51		205.47	Nb(IV)–O
		455.56	Ti(II)–O	4.61		204.76	Nb(II)–O
	V $2p_{3/2}$	517.26	V(V)–O	35.68	Ce $3d_{5/2}$	882.78	Ce(IV)
		515.98	V(IV)–O	28.22		881.01	Ce(III)
		515.18	V(III)–O	14.48		75.06	Al(III)–O
		514.18	V(III)–OH	21.62	Al $2p$	74.08	Al(III)–N
6 W	Ti $2p_{3/2}$	458.64	Ti(IV)–O	58.42	Nb $3d_{5/2}$	207.21	Nb(V)–O
		457.07	Ti(IV)–OxNy	14.78		205.59	Nb(IV)–O
		456.11	Ti(III)–OxNy	18.73		204.87	Nb(II)–O

		455.22	Ti(III)–N	8.06		204.25	Nb(V)–N
	V 2p _{3/2}	517.24	V(V)–O	30.13	Ce 3d _{5/2}	882.72	Ce(IV)
		515.99	V(IV)–O	15.73		881.25	Ce(III)
		515.11	V(III)–O	13.65	Al 2p	75.19	Al(III)–O
		514.46	V(III)–O _x N _y	20.71		74.29	Al(III)–N
		513.55	V(III)–N	19.78			
12 W	Ti 2p _{3/2}	458.62	Ti(IV)–O	41.14	Nb 3d _{5/2}	207.02	Nb(V)–O
		457.21	Ti(IV)–O _x N _y	7.85		205.12	Nb(IV)–O
		455.95	Ti(III)–O _x N _y	26.50		204.31	Nb(V)–N
		454.90	Ti(III)–N	24.50		203.65	Nb(III)–N
	V 2p _{3/2}	516.64	V(V)–O	15.70	Ce 3d _{5/2}	882.57	Ce(IV)
		515.79	V(IV)–O	7.79		880.85	Ce(III)
		514.75	V(III)–O	28.65	Al 2p	74.27	Al(III)–N
		514.01	V(III)–O _x N _y	2.12		71.15	Al(0)
		513.14	V(III)–N	45.74			

Both metal oxynitride and nitride component peaks systematically emerged in the low binding energy bands of the 6 W sample, consistent with the presence of both tetragonal rutile oxide and cubic rock salt nitride structures in the WAXS data (Fig. 15). The XPS spectrum of 12 W sample displayed the metal-nitride component peaks in the Ti 2p, Nb 3d, V 2p and Al 2p core levels most prominently, corroborating the sample had a single cubic rock salt metal oxynitride structure (denoted as TiNbAlCeVO_xN_y).

Although the oxide and nitride component peaks of Ce 3d could not be resolved, the small increase in Ce(III)/Ce(IV) ratio may imply formation of CeN after laser annealing at 12 W. XPS composition analysis indicated that the metal constituent ratios remained almost unchanged for all TiNbAlCeV-based samples after irradiation at different powers (see Table 7), in contrast to the AuPdFeCuNi HEA-NPs counterpart (see Table 2). This could be attributed to the short heating time (0.25 ms) that kinetically inhibited metal atom diffusion and improved the thermodynamic stability with electronegative oxygen and nitrogen in the crystal lattice.

Laser irradiation at higher powers of 6 and 12 W, however, enabled carbothermal reduction and nitridation, with the polyacrylonitrile-derived CNF substrate acting as an *in situ* nitrogen source to substitute oxygen and thereby promote the transformation of the precursor mixture into cubic rock salt TiNbAlCeVO_xN_y NPs.

Table 7. XPS chemical analysis of ratios of metallic components in TiNbAlCeV-based samples after laser irradiation at 2, 6 and 12 W, respectively, all for 0.25 ms.

Sample	Constituent Metals (%)				
	Ti	Nb	Al	V	Ce
2 W	19.44	30.38	17.03	19.36	13.80
6 W	19.34	23.49	18.59	21.02	17.57
12 W	21.03	32.54	11.24	21.27	13.92

Example 4d: Characterization of TiON

Figs. 19a-c show a series of TEM and HAADF STEM-EDX micrographs of TiON NPs with a hollow particle morphology after laser irradiation of the precursor mixture of Example 2i at 6 W laser power for 2.5 ms heating dwell. The formation of a new particle morphology is attributed to Kirkendall effect and enhanced atomic diffusion kinetics during longer laser annealing dwells.

Example 4e: Characterization of CrMnFeCoNi and CrFeCoNiPd

Additional nanoparticles comprising new metal combinations of CrMnFeCoNi (Cantor HEA) and CrFeCoNiPd (Pd-modified Cantor HEA) were formed using the same laser annealing process as described in Example 3, with laser parameters of 2 W for 2.5 to 250 ms dwells were performed. The WAXS spectrum of CrFeCoNiPd (Pd modified Cantor HEA-NP) in Fig. 20B formed at 2.5 ms dwell time has a shoulder peak on the right-hand side of the primary peak with a rather significant peak position difference of ~4%, suggestive of a secondary crystalline phase. The increase in the intensities of the shoulder peak after irradiation for longer dwells of 25 and 250 ms indicated improved stability of the second crystalline phase.

In contrast, no shoulder peak was observed in the WAXS spectrum of CrMnFeCoNi (Cantor HEA) after irradiation at 2.5 ms (see Fig. 20A). A minor peak shift of 1.6% was observed for the CrMnFeCoNi (Cantor HEA) samples after irradiation at 25 and 250 ms that could be attributed to presence of residual stresses in the crystal lattices. Hence, this supports the presence of a dual crystalline phase in the Pd modified Cantor HEA-NPs and corroborates the influence of laser-induced supercooling kinetics, atomic size and electronegativity differences (Figs. 20a-b).

Example 4f: AgCu, AgCuFe, AuCuCoFe

The method disclosed in Example 3 was also used to synthesise other nanoparticles with 2, 3 and 4 metal elements as a proof-of-concept.

In summary, the mixture-coated substrates of Examples 2e, 2f and 2g were subjected to the method as disclosed in Example 3, with laser annealing parameters of 2 W and a dwell time of 0.25 ms. The HAADF-STEM and EDS images of the three samples are shown in Figs. 5c, 5d and 5e respectively.

In short, the successful synthesis of binary, ternary, quaternary metal nanoparticles, on top of the quinary and mono nanoparticles as discussed earlier indicate that the presently disclosed method for producing nanoparticles is highly versatile and can be applied to any number of metal elements as required.

Example 5: Absolute temperature calibrations and FEA simulations using platinum (Pt) as reference

To relate the laser heating protocols to “universal” parameters (e.g., temperature, pressure), absolute calibrations and finite element modeling (FEA) were performed with platinum as the reference to convert the millisecond laser annealing characteristics to peak temperature (at laser beam centre) and obtain the corresponding cooling rate melt durations (Fig. 24a and Table 8). The optical absorbance (A) of (1) sputter-deposited 60–70 nm thick Pt film on glass, (2) ~100–120 nm thick AuPdCuFeNi metal precursor film on glass, and (3) ~50 μ m thick PAN-derived CNF substrate was measured. The absorption coefficient (α) values of Pt, AuPdCuFeNi precursor, and CNF carbon were calculated using eq. S1 where d is the film thickness and A is the absorbance at 532 nm. The absorbance curves and absorption coefficient values of the respective samples were plotted in Fig. 24a.

$$\alpha = \frac{2.303A}{d} \quad (S1)$$

Pt was chosen as the temperature calibration reference as its optical properties are close to the metal precursors. It should be further noted that Pt results are the upper limit on the simulated peak laser temperatures of the metal precursors. For absolute temperature calibrations, 60–70 nm thick Pt films were sputter-deposited on 330 μ m thick carbon substrates (AvCarb GDS2210). The Pt/carbon samples were then heated by a single laser irradiation at laser powers of 0.1 to 12 W for dwells of 0.25 to 250 ms. Melt and solidification of the Pt film was observed visually in the scanned lines. For each annealing dwell, the lowest laser power that induced Pt melt line was determined and calibrated as the melting point of Pt at 1768 °C. Figs. 24b-f show the simulated temperature profiles of Pt/carbon samples after laser irradiation at 2 W for different dwell times.

For 2D, the FEA simulation model is a Pt/carbon substrate with a 2.5 mm long by 70 nm thick Pt overlayer on a 2.5 mm long by 0.33 mm thick carbon substrate that is placed in contact with a 100 mm long by 20 mm thick aluminum block (dynamic linear stage). The 532 nm laser heat source, Q (Equations S2 and S3), was modelled as a Gaussian line with beam profile r_x and r_y of 340 μm and 85 μm , respectively, where $r = (1.699 \times FWHM) / 2$. It is reasonable to assume the Pt/carbon substrate is thermally isotropic and the Pt overlayer fully absorbs the laser photons. All surfaces were subjected to surface-to-ambient radiation using eq. S4. The simulated peak temperature T of Pt/carbon substrate was computed using eq. S5. The heat capacity of the carbon substrate was calculated using eq. S6. All other materials properties are summarized in Table 8 and constants used summarised in Table 9.

$$Q = (1 - R) \left(\frac{2Pa}{\pi r_x r_z} \right) \exp \left(\frac{-(r_{focus})^2}{2} \right) \exp(-\alpha y) \quad (S2)$$

$$r_{focus} = \frac{4 \left(x - \frac{r_x t}{t_{dwell}} \right)^2}{r_x r_z} \quad (S3)$$

$$n \cdot (k \nabla T) = \varepsilon \sigma (T_0^4 - T^4) \quad (S4)$$

$$Q = \rho C_p \frac{\partial T}{\partial t} - \nabla(k \nabla T) \quad (S5)$$

$$C_{p,carbon} = (1.062 \times 10^{-6})T^3 - (2.983 \times 10^{-3})T^2 + (3.2)T + 639.66 \quad (S6)$$

Table 8. Simulated laser annealing characteristics of MC inorganic NPs

Power (W)	Dwell Time (ms)	T_{peak} ($^{\circ}\text{C}$)	Melt Duration (ms)	Cooling Rate (K/s)
0.6	2.5	1445	14	5.5×10^4
2	0.25	1830	2.5	1.2×10^5
2	2.5	3165	33	4.8×10^4
2	25	3580	270	1.1×10^4
2	250	3590	2700	1.3×10^3
3	0.25	2410	4.6	7.6×10^4
4	0.25	2830	6.8	5.4×10^4
6	0.25	3430	11	6.0×10^4

Table 9. Constants used in the FEA simulation

Property	Pt	Carbon	Al	Laser
R , reflectance	0.633			
α (m^{-1}), absorption coefficient	4.9×10^7			
r_x (μm), beam width (FWHM)				50
r_z (μm), beam length (FWHM)				200
P (W), laser power				0.5–2
t_{dwell} (ms), laser annealing dwell				0.25–250
T_0 (K), ambient temperature	293.15	293.15	293.15	
ρ (kg m^{-3}), density	21450	53	2700	
k ($\text{W m}^{-1} \text{K}^{-1}$), thermal conductivity	71.6	0.35	237	
C_p ($\text{J K}^{-1} \text{kg}^{-1}$), specific heat capacity	133	eq S6	904	
ε , surface emissivity	0.47	1	0.09	

Example 6: New material properties

Changing laser annealing parameters has also provided NPs with new compositions, structures and materials properties.

Magnetic property

It was observed that quinary AuPdFeCuNi NPs annealed at 2 W for longer dwells (to 25 ms from 0.25 ms) exhibited magnetic properties (**Figs. 26a-b**). It was observed that the CNF substrate with NPs annealed with 0.25 ms dwell time was not attracted towards the magnet after 10 seconds (**Fig. 26a**). However, when the dwell time was increased to 25 ms, the substrate containing the NPs were observed to gradually move towards the magnet and reached the edge of the beaker with the magnet at $t = 18$ seconds (**Fig. 26b**). It is hypothesised that the nanoparticles were magnetic because of the increased concentrations of ferromagnetic Fe and Ni elements when the dwell time was increased from 0.25 ms to 25 ms.

Thus, it is shown that changing the dwell time of the laser annealing process can impart magnetic properties to the nanoparticles of the present invention.

Nanoparticle morphology

Laser annealing to generate AuPdFeCuNi NPs at a far lower laser power of 0.6 W for 2.5 ms (~1445 °C) instead generated AuPdFeCuNi NPs with a Pd-core and an AuFeCuNi-shell heterostructure (**Figs. 27a, 27b and 27c**). This is attributed to the early solidification of highest melting point Pd, forming the NP core, followed by a slower solidification of the remaining metals forming the shell.

Hence, it is shown that further changing the annealing parameters to achieve a lower annealing peak temperature can result in nanoparticles with new compositions and morphologies.

Example 7: Laser annealing on various substrates

The laser annealing process of the present invention is also versatile for high-temperature processing of materials on multiple solid substrates such as glass. To show the versatility, laser annealing was performed on the precursor-coated substrate of Example 2a-ii. Laser annealing parameters were set at 2 W for 25 ms (**Figs. 28a-b**). **Fig. 22a** shows the bright-field TEM and elemental EDS images of the same AuPdCuFeNi NPs, while **Fig. 22b** shows the Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) data of the same AuPdCuFeNi NPs as produced.

The results show the resulting NPs have a single fcc phase and nominal atomic composition of 24% Au, 24% Pd, 22% Cu, 19% Fe and 11% Ni. The successful formation of AuPdFeCuNi NPs as seen in the SEM image of **Fig. 28b** indicate that the presently disclosed invention can be applied to other substrates.

Example 8: Transferring HEA-NPs onto further substrates

The nanoparticles of the present invention can also be easily transferred onto other substrates for further applications. To prove the concept, AuPdFeCuNi HEA-NPs were first synthesised on a CNF substrate according to the method as disclosed in Examples 2a-ii and 3 at 2 W laser power for 0.25 ms dwell. After laser annealing, the CNF substrate coated with the HEA-NPS were removed from the substrate using tape (**Fig. 29a**), and subsequently transferred to a flexible poly(ethylene terephthalate) substrate (see **Fig. 29b**).

Hence, it is shown that the nanoparticle-coated substrates of the present invention may be easily transferred onto further substrates for further applications.

Example 9: NP catalyzed growth of carbon nanotubes by laser annealing

A AuPdCuFeNi precursor coated-CNF substrate was prepared according to Example 2a. The substrate was then subjected to laser annealing according to Example 3 under nitrogen with laser power of 10 W and time dwell of 1 ms.

At the above-mentioned laser annealing parameters, it was observed that the AuPdCuFeNi NPs were able to augment the growth activity of carbon nanotubes (CNTs) with the CNF substrate as *in situ* carbon source and laser irradiation as stimulus. Fig. 30b shows a TEM image of simultaneous generation of 30-nm-diameter CNTs with AuPdFeCuNi NPs (Fig. 30a) as the catalyst after irradiation at 10 W for 1 ms (Figs. 30a-c). The HR-TEM image in Fig. 30c confirmed highly aligned clusters of graphitic sheets in the laser-induced CNTs.

Figs. 30a and 31a-c further show the TEM, HAADF-STEM and EDS elemental mapping analysis images of the synthesised CNTs, as well as the AuPdCuFeNi NPs formed.

Hence, it is shown the NPs of the present invention may be used to catalyse the formation of CNTs, in particular to catalyse the *in situ* formation of CNTs during the laser annealing process to produce the same NPs.

Example 10: Hydrogen Evolution Reaction (HER)

The NPs of the present invention were also tested to show their suitability as catalysts in driving the Hydrogen Evolution Reaction (HER).

The laser-induced Pd-NP-CNF and AuPdCuFeNi-NP-CNF samples were synthesized as according to Example 3 at 2 W laser power for 0.25 ms dwell, and carefully grounded into fine powder forms.

For the respective working electrodes, ~0.5 mg of the finely powdered NP-CNF, 4 μ L of Nafion (5 wt%), 0.125 mg of Super P and 40 μ L of ethanol were mixed and ultrasonicated for 60 min to form a homogenous ink. Separately, the mass of the polished glassy carbon electrode (GCE) substrates of 5 mm diameter (geometric area of 0.196 cm²) was measured, followed by loading of 4 μ L aliquots of the NP-CNF catalyst ink on each GCE by drop casting. The NP-CNF working electrodes were dried for 15 min under ambient conditions and then transferred into a low humidity dry box for additional drying of another 120 min. The dried loadings of the Pd-NP-CNF and AuPdCuFeNi-NP-CNF catalysts were calculated to be ca. 0.09 and 0.05 mg, respectively. All electrochemical measurements were conducted using a standard three-electrode system that comprised the catalyst-loaded GCE as working electrode, a Pt-metal counter electrode and a Hg/HgO reference electrode. The electrocatalytic activities of the working electrodes in the HER experiments were measured by linear sweep voltammetry (LSV) in 1 M KOH electrolyte at 25 °C under stirring (1000 rpm) using a PARSTAT MC 1000 station. The scan rate was 2 mV/s. The electrochemical data were reported after applying offset potential corrections against a reversible hydrogen electrode (RHE) and accounting for internal resistance. The negative-wave sweeps were presented until -1.0 V (versus RHE). For the electrochemical stability experiments, long-term chronopotentiometry measurements were performed at a constant load of 10 mA/cm² with the Pd-NP-CNF-loaded and AuPdCuFeNi-NP-CNF-loaded GCE working electrodes with a scan rate of 100 mV/s in 1 M KOH electrolyte at 25 °C under stirring (1000 rpm) over 12 h.

Fig. 33 shows the polarization curves of four HER reactions performed in 1 M KOH (bare glassy carbon electrode, bare CNF substrate, mono-Pd-CNF and AuPdFeCuNi NP-CNF). The AuPdFeCuNi HEA-NP composite required a slightly higher overpotential of -0.35 V (compared to -0.31 V for the electrode comprising the mono-Pd NP-CNF composite) to drive a current density of 10 mA/cm²,

However, it was also observed that the AuPdFeCuNi HEA-NP composite demonstrated the most stable electrochemical activity. This was shown in Fig. 34 where the AuPdFeCuNi HEA-NP composite maintained the lowest overpotential of -0.36 V after 12 h in order to drive 10 mA/cm² as compared to a higher overpotential of -0.39 V as required by the mono-Pd NP-CNF composite. The faster deterioration of the mono-Pd NP-CNF composite activity was likely due to surface oxidation; these results suggest that

the transitional metal components in the HEA-NPs conferred surprising stability against surface oxidation to the catalysts.

Hence, it is shown that the nanoparticles of the present invention can be used in catalysing the HER.

Example 11: Antibacterial Properties

The antibacterial efficiencies of the nanoparticles of the present invention were also tested.

In summary, uncoated CNF substrate, 0.05 M AgNO₃/CuCl₂-coated-CNF composite and AgCu-NP-CNF composite were evaluated against *E. coli*. The AgCu-NP-CNF composite was generated by laser annealing the precursor AgNO₃/Cu(NO₃)₂-coated-CNF of Example 2g according to the laser annealing process as described in Example 3, with parameters at 2 W for 0.25 ms.

An overnight culture of *E. coli* bacteria in Luria-Bertani (LB) broth was prepared. The bacterial suspension was first incubated at 37 °C for 3 h and then diluted to 5×10⁵ CFU/mL with the LB broth. The *E. coli* suspension was transferred into a 48-well plate (Greiner Bio-One) where each well contained a 1 mL aliquot volume. After immersing the 5 mm × 5 mm samples, the well plate was incubated at 37 °C for another 24 h under static conditions for bacteria growth. The antibacterial effects of the samples were characterized by the optical density (OD) method and live/dead fluorescence staining to determine the density of planktonic bacteria surrounding the films as well as bacteria attached on the samples, respectively. OD measurements were obtained at 600 nm using a spectrophotometer, once before the plate incubation to determine the appropriate dilution factor for the bacteria culture, and then again after the plate incubation to determine the bacterial density remaining in each well. For the live/dead fluorescence staining, the wells containing the samples, together with the cell control wells, were washed twice with filtered 0.85% NaCl solution, and then stained with SYTO9 and PI (BacLight Live/Dead Bacterial Viability Kit, Molecular Probes) in a ratio of according to the manufacturer's instructions. The samples were mounted on a glass slide and observed under a fluorescence microscope (Zeiss Axio Observer Z2), with filter sets of 488/500 and 488/635 for SYTO9 and PI, respectively.

Fig. 35 shows the fluorescence images of green-colored live *E. coli* cells dyed with SYTO-9 in the three wells of the tested substrates. Absence of PI-stain (red fluorescence confirmed that the CNF substrate alone was non-bactericidal. It was observed that the AgNO₃/CuCl₂-coated-CNF composite exhibited some levels of antibacterial properties, as indicated by the mixed green and red fluorescence, albeit at lower intensities. It was hypothesised that the Ag⁺ and Cu²⁺ released by the salts were responsible for the inhibition of bacterial growth by rupturing the *E. coli* cell membranes. In contrast, the AgCu-NP-CNF composite exhibited the strongest antibacterial property, corroborated by the lack of fluorescent signals. This strongly suggested that the AgCu-NP-CNF composite samples could synergistically exert a potent antimicrobial and antibiofouling action on the *E. coli*. Optical density measurements (Fig. 36a) also indicated that the *E. coli* cellular metabolic activity was significantly suppressed by about 14-fold in the AgCu-NP-CNF composite sample as compared to the other two experiments. It is hypothesised that the AgCu-NPs provided a targeted and sustained release of Ag⁺ and Cu²⁺ ions into *E. coli*, inducing release of reactive oxygen species to cause DNA damage. Further experiments using the AuPdFeCuNi NPs formed on CNF substrate using the presently disclosed annealing method at 2 W laser power for 0.25 ms dwell (abbreviated LAM³ix as described Example 3), AuPdFeCuNi NPs formed using a pulsed laser ablation method, as well as the CNF scaffold as a negative control were tested, with results shown in Fig. 36b. In the pulsed laser ablation method, the precursor mixture of Example 2a was subjected to laser ablation (abbreviated as PLA) using a single 1.5 ns pulsed Nd:Yag laser (532 nm wavelength) at 2 W for a total of three times. The focused PLA laser beam size was 0.1 mm by 0.1 mm.

The nanoparticles formed by the presently disclosed laser annealing process exhibited the best antibacterial response against *E. coli* as compared to the other samples after incubation at 37 °C for 24 hours, indicating that the presently disclosed laser annealing method was able to impart unique

antimicrobial properties to the synthesised nanoparticles, as compared to conventional laser ablation processes.

Hence, it is amply demonstrated that the nanoparticles of the present invention exhibit anti-microbial properties, and can be used as an effective nano-enabled anti-microbial platform.

Industrial Applicability

The present invention relates to a method of producing multiphasic crystalline nanoparticles. The method can produce nanoparticles with multiple phases in the same nanoparticle, a phenomenon that usually observed only in bulk metals. The method of the present invention also be used to form nanoparticles with any combination of metals as it avoids the need to first form solid target alloys of the combination of metals prior to laser irradiation. The presently disclosed method can also work with any metal precursor as laser irradiation may be performed under air or nitrogen. The nanoparticles produced by the method of the present invention are also crystalline in nature.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

CLAIMS

We claim:

1. A method of producing multiphasic crystalline nanoparticle(s), comprising:
 - a. preparing a mixture of at least one metal precursor and solvent;
 - b. applying the mixture to a substrate; and
 - c. subjecting the mixture to laser irradiation for a duration of about 0.01 ms to about 500 ms, at a power of about 0.1 W to about 100 W to reach peak temperatures of 250 to 4000 °C, wherein step (c) comprises laser irradiating a mixture which does not comprise pure metal.
2. The method of claim 1, wherein the multiphasic crystalline nanoparticle(s) comprises at least two phases and/or crystal systems selected from the group consisting of face-centred cubic (FCC), body-centred cubic (BCC), cubic rock salt, tetragonal, rutile tetragonal, hexagonal, orthorhombic, rhombohedral, monoclinic or triclinic crystal systems.
3. The method of claim 1 or 2, wherein the mixture comprises at least four metal precursors.
4. The method of any one of claims 1-3, wherein the metal precursors are selected from the group consisting of metal salts, metal oxides, metal nitrates, metal alkoxides, and combinations thereof.
5. The method of any one of claims 1-4, wherein the metal of the metal precursors is selected from the group consisting of Li, Be, Na, Mg, K, Ca, Rb, Sr, Ba, Fr, Ra, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Ru, Rh, Pd, Ag, Cd, W, Re, Os, Ir, Pt, Au, Hg, Nb, Ce, Al, Cs, Si, Ge, Sn, Pb and combinations thereof.
6. The method of any one of claims 1-5, wherein the atomic sizes of the metal of the metal precursors differ by about 5% to about 15%.
7. The method of any one of claims 1-6, wherein step (c) is performed with a laser having a wavelength from about 200 nm to about 10600 nm.
8. The method of any one of claims 1-7, wherein step (c) is performed in an atmosphere selected from the group consisting of ambient air, unreactive gas, N₂, Ar, He, O₂, Ne, Kr, Rn, and mixtures thereof.
9. The method of any one of claims 1-8, wherein the substrate comprises reduced graphene oxide, graphene oxide, cellulose, chitosan, carbon, carbon nanofiber, silicon, glass, quartz, sapphire, and/or polyacrylonitrile.
10. The method of any one of claims 1-9, wherein the concentration of each metal precursor in the mixture of step (a) is from about 0.01 M to about 10 M.
11. The method of any one of claims 1-10, wherein the solvent is selected from the group consisting of water, alcohols, ketones, ethers, amides, lactones, lactams, sulfones, sulfoxides, alkanes, alkenes, and combinations thereof.
12. The method of any one of claims 1-11, wherein step (b) comprises dropcasting the mixture onto the substrate or immersing the substrate in the mixture.
13. The method of any one of claims 1-12, wherein the method produces multiphasic crystalline nanoparticle(s) of AuPdCuFeNi, CrMnFeCoNi, CrFeCoNiPd, TiNbAlCeV, TiNbAlCeVO, TiNbAlCeVON, TiNbAlCeVN, AuCuCoFe, AgCu or AuCuFe.
14. The method of any one of claims 1-13, wherein the method comprises:
 - a. preparing a mixture of at least two metal precursors selected from the group consisting of salts, oxides, nitrates and/or alkoxides of Au, Pd, Cu, Fe, Ni, Ti, Nb, Al, Ce, V, Cr, Mn, Co, Cs, Si, Ge, Sn, and Pb;

- b. applying the mixture to a substrate; and
 - c. subjecting the mixture to laser irradiation for a duration of about 0.25 ms to about 500 ms, at a power of about 0.5 W to about 12 W to reach peak temperatures of about 1000 °C to about 4000 °C,
wherein step (c) comprises laser irradiating a mixture which does not comprise pure metal.
15. A multiphasic crystalline nanoparticle produced by the method of any one of claims 1-14.
16. A multiphasic crystalline nanoparticle comprising at least four metals selected from the group consisting of Li, Be, Na, Mg, K, Ca, Rb, Sr, Ba, Fr, Ra, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Ru, Rh, Pd, Ag, Cd, W, Re, Os, Ir, Pt, Au, Hg, Nb, Ce, Al, Cs, Si, Ge, Sn, Pb and combinations thereof, and at least two phases/and or crystal structures selected from the group consisting of FCC, BCC, cubic rock salt, tetragonal, rutile tetragonal, hexagonal, orthorhombic, rhombohedral, monoclinic or triclinic crystal systems.
17. The nanoparticle of claim 16, wherein the nanoparticle has an average particle diameter from about 3 nm to about 500 nm.
18. The nanoparticle of claim 16 or 17, wherein the nanoparticle has an average lattice spacing from about 0.1 nm to about 0.5 nm.
19. The nanoparticle of any one of claims 16-18, wherein the nanoparticle has an average lattice constant from about 0.1 nm to about 0.9 nm.
20. The nanoparticle of any one of claims 16-19, wherein the nanoparticle is selected from the group consisting of AuPdCuFeNi, CrMnFeCoNi, CrFeCoNiPd, TiNbAlCeV, TiNbAlCeVO, TiNbAlCeVON, TiNbAlCeVN, and AuCuCoFe.
21. The nanoparticle of any one of claims 16-20, wherein the nanoparticle is AuPdCuFeNi and comprises FCC and BCC phases.
22. The nanoparticle of any one of claims 16-20, comprising five metals selected from Ti, Nb, Al, Ce and V, and at least a cubic rock salt phase and at least a rutile tetragonal crystal system.
23. A multiphasic crystalline nanoparticle of any one of claims 15 to 22, for use in inhibiting bacterial growth.