

METAL-CONTAINING PARTICLES, PROCESSES FOR THEIR
PREPARATION, AND USES THEREOF

Technical Field

5 The present invention generally relates to metal-containing particles, processes for their preparation, and uses thereof. The metal-containing particles may be useful in enhancing the thermal conductivity of thermally conductive compositions.

10 Background

In tropical countries, there is a great demand to develop a passive-cooling technology for effectively removing indoor heat without expending electrical energy, especially for highly glazed buildings.

15 Phase change materials have been considered as promising materials that can cool down ambient temperatures without consuming electrical energy. Phase change materials are materials that absorb surrounding heat through latent of fusion and undergo phase changes, typically from solid phase to liquid phase. In such a way, ambient temperatures may be maintained at a cooler temperature. Phase change materials are normally used in buildings for temperature control management by providing a passive free cooling of indoor room temperature and time-shifting of air-conditioned cooling loads.

25 However, commercially available phase change materials suffer from low thermal conductivity. Low thermal conductivity undesirably hinders the thermal energy transfer and significantly reduces heat absorption/release capability. Hence, this diminishes the thermal energy-storage capacity of a phase change material. For example, inorganic phase change materials, such as hydrated calcium chloride ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) and

hydrated sodium phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) salts, possess high thermal energy-storage capacities, but they suffer from low thermal conductivities of ~ 0.54 W/mK and ~ 0.514 W/mK, respectively.

5 Consequently, phase change materials may include a filler material that is thermally conductive to enhance the thermal conductivity of the phase change material.

 Nanostructured metals generally show high thermal conductivity. Known methods of producing nanostructured
10 metals involve atomization, electrolysis, hydrometallurgy, or solid state reduction. However, metal particles produced by these methods easily oxidize upon air exposure, significantly reducing their thermal conductivity when compared with their metallic state.

15 Furthermore, processes to form nanostructured metals are generally expensive due to the reactants used. These processes may also be time-consuming and difficult due to the multitude of steps involved.

 Another problem with known processes to form
20 nanostructured metals is that they may be toxic and non-environmentally friendly.

 There is therefore a need to provide nanostructured metals and processes of making them that overcome, or at least ameliorate, one or more of the disadvantages
25 described above.

 There is also need to provide phase change materials that have high thermal conductivity.

Summary

30 As disclosed herein, there is provided a process for producing a metal-containing particle, the process comprising:

a) forming a reaction mixture comprising (i) a metal salt, and (ii) a reaction medium comprising a capping agent, and

5 b) subjecting the reaction mixture to heat conditions to enable the formation of elemental metal, thereby forming said metal-containing particles.

In a first aspect, there is provided a process for producing transition metal-containing particles, the process comprising:

10 a) forming a reaction mixture comprising (i) a transition metal salt, and (ii) a reaction medium comprising a capping agent,

b) subjecting the reaction mixture to heat conditions to enable the formation of elemental transition
15 metal, thereby forming the transition metal-containing particles, and

c) recycling the reaction medium for reuse in step (a).

Advantageously, the capping agent may also function
20 as a reducing agent. Therefore, the disclosed process may not require the use of other reducing agent(s) such as strong reducing agents, glucose or ascorbic acid. Known reducing agents may be expensive and/or toxic. Therefore, the disclosed process may advantageously be efficient,
25 cost-effective, non-toxic and environmentally friendly.

Also advantageously, the capping agent may also function as a surface-protecting agent. Therefore, the disclosed process may also not require surface-protecting agents which may also be expensive and/or toxic.
30 Therefore, the disclosed process may be efficient, cost-effective, non-toxic and environmentally friendly.

Further advantageously, the reaction medium of the disclosed process may be reused. The reusability of the

Examination Report

Application No.

11201510700V

I. Basis of the report

1. This report has been drawn on the basis of:

- ☒ the **description**,
 page(s) 1, 5-37 as originally filed
 page(s) 2, 3a filed as amendment sheet(s) dated 22/06/2016
 page(s) 4a filed with the response to the written opinion dated 04/01/2017
 page(s) 3, 4 filed with the response to the written opinion dated 01/08/2017
- ☒ the **claim(s)**,
 no. 1-29 filed with the response to the written opinion dated 01/08/2017
- ☒ the **drawing(s)**,
 page(s) 1-9 as originally filed
- ☒ and in consideration of the **response to the written opinion(s)** dated
 04/01/2017
 01/08/2017

2. ☐ This report has been established based on the exclusion of additional matter beyond the earlier application, as indicated in the supplemental box.

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the supplemental box.

4. Additional observations, if necessary:

reaction medium reduces the overall production cost of the disclosed metal-containing particles.

Also advantageously, the capping agent may be derived from naturally occurring compounds found in
5 various animal and vegetable fats and oils. The disclosed process therefore may involve low-cost, abundant and environmentally benign reaction materials.

Further advantageously, the disclosed process may involve only a single heating step, resulting in a
10 process that is straightforward and cost-effective.

In a second aspect, there is provided a process for producing a thermally conductive composition, the process

comprising:

- a) forming a reaction mixture comprising (i) a transition metal salt, and (ii) a reaction medium comprising a capping agent,
- 5 b) subjecting the reaction mixture to heat conditions to enable the formation of elemental transition metal, thereby forming transition metal-containing particles,
- c) recycling the reaction medium for reuse in step
- 10 (a), and
- d) adding the transition metal-containing particles produced by the process of steps (a) to (c) to a heat transfer medium.

Advantageously, the thermally conductive composition
15 possesses enhanced thermal conductivity when compared to a composition without the disclosed metal-containing particles.

In a third aspect, there is provided a thermally conductive composition comprising a heat transfer medium
20 and a transition metal-containing particle produced by a process as defined above.

Advantageously, the thermal conductivity of the thermally conductive composition may be greatly enhanced when doped with the disclosed metal-containing particles.

25

Definitions

The following words and terms used herein shall have the meaning indicated.

As used herein, the term "metal-containing
30 particles" include, but are not limited to, elemental metal particles, metal particle-based composites, fine particles comprising metal, metal microparticles, metal microwires, metal microrods, metal nanoparticles, metal nanowires, metal nanorods, transition metal particles,

transition metal microparticles, transition metal microwires, transition metal microrods, transition metal nanoparticles, transition metal nanowires and transition metal nanorods.

As used herein, the term "micro" is to be
5 interpreted broadly to include dimensions between about 1 micron to about 500 microns.

As used herein, the term "nano" is to be interpreted broadly to include dimensions less than about 1000 nm.

As used herein, the term "capping agent" refers to a
10 molecule possessing a functional group capable of

absorbing or binding to the surface atom of a material, such as metal-containing particles, by an ionic or covalent bond. This may include a compound that may protect the surface of the material, avoiding oxidation, agglomeration, degradation and preserving the properties of the material. The capping agent may further preferentially interact and adhere to a lateral surface of a growth particle, such that the capping agent confines the lateral surface from growing and encourages a cross section surface of the particle to form.

As used herein, the term "reducing agent" refers to a chemical agent capable of causing the reduction of another substance as it itself is oxidized, i.e. a chemical agent capable of donating an electron in an oxidation-reduction reaction. The term "strong reducing agents" refers to reducing agents that easily lose (or donate) electrons and may include, for example, sodium boron hydride, dimethylamineborane, hydrazine, glucose and ascorbic acid.

As used herein, the term "heat transfer medium" refers to gaseous or liquid fluids, solids, semi-solids, liquids, or phase change heat transfer materials, and includes materials which may be solid at room temperature, but may undergo a phase transition at certain temperatures.

As used herein, the term "phase change material" refers to a material that undergoes a phase change, typically between the liquid and solid phases.

The term "transition metal" describes, for example, any metal in Groups III through VII of the periodic table, for example, elements 21 through 30 (scandium through zinc), 39 through 48 (yttrium through cadmium), 57 through 80 (lanthanum through mercury), and 89 through 103 (actinium through lawrencium). Useful transition

metals include, for example, copper, iron, gold, silver, cobalt, ruthenium, rhodium, palladium, iridium, platinum, osmium, nickel, tin, gallium and zinc.

As used herein, the term "alkyl" includes within its meaning monovalent ("alkyl") and divalent ("alkylene") straight chain or branched chain saturated aliphatic groups having from 1 to 35 carbon atoms, eg, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34 or 35 carbon atoms. For example, the term alkyl includes, but is not limited to, methyl, ethyl, 1-propyl, isopropyl, 1-butyl, 2-butyl, isobutyl, tert-butyl, amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, 2-ethylpentyl, 3-ethylpentyl, heptyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, 5-methylheptyl, 1-methylheptyl, octyl, nonyl, decyl, undecyl, dodecyl and the like. Alkyl groups may be optionally substituted.

As used herein, the term "alkenyl" refers to divalent straight chain or branched chain unsaturated aliphatic groups containing at least one carbon-carbon double bond and having from 2 to 35 carbon atoms, e.g., 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34 or 35 carbon atoms. For example, the term alkenyl includes, but is not limited to, ethenyl, propenyl, butenyl, 1-butenyl, 2-butenyl, 2-methylpropenyl, 1-pentenyl, 2-pentenyl, 2-methylbut-1-

enyl, 3-methylbut-1-enyl, 2-methylbut-2-enyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 2,2-dimethyl-2-butenyl, 2-methyl-2-hexenyl, 3-methyl-1-pentenyl, 1,5-hexadienyl and the like. Alkenyl groups may be optionally substituted.

5 As used herein, the term "alkynyl" refers to trivalent straight chain or branched chain unsaturated aliphatic groups containing at least one carbon-carbon triple bond and having from 2 to 35 carbon atoms, e.g., 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 10 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34 or 35 carbon atoms. For example, the term alkynyl includes, but is not limited to, ethynyl, propynyl, 1-butyne, 2-butyne, 1-pentyne, 2-pentyne, 1-hexyne, 2-hexyne, 3-hexyne, 3-methyl-1-pentyne, and 15 the like. Alkynyl groups may be optionally substituted.

The term "optionally substituted" as used herein means the group to which this term refers may be unsubstituted, or may be substituted with one or more groups other than hydrogen provided that the indicated 20 atom's normal valency is not exceeded, and that the substitution results in a stable compound. Such groups may be, for example, halogen, hydroxy, oxo, cyano, nitro, alkyl, alkoxy, haloalkyl, haloalkoxy, arylalkoxy, alkylthio, hydroxyalkyl, alkoxyalkyl, cycloalkyl, 25 cycloalkylalkoxy, alkanoyl, alkoxycarbonyl, alkylsulfonyl, alkylsulfonyloxy, alkylsulfonylalkyl, arylsulfonyl, arylsulfonyloxy, arylsulfonylalkyl, alkylsulfonamido, alkylamido, alkylsulfonamidoalkyl, alkylamidoalkyl, arylsulfonamido, arylcarboxamido, 30 arylsulfonamidoalkyl, arylcarboxamidoalkyl, aroyl, aroylalkyl, arylalkanoyl, acyl, aryl, arylalkyl, alkylaminoalkyl, a group R^xR^yN- , $R^xOCO(CH_2)_m$, $R^xCON(R^y)(CH_2)_m$, $R^xR^yNCO(CH_2)_m$, $R^xR^yNSO_2(CH_2)_m$ or $R^xSO_2NR^y(CH_2)_m$ (where each of R^x and R^y is independently

selected from hydrogen or alkyl, or where appropriate R^xR^y forms part of carbocyclic or heterocyclic ring and m is 0, 1, 2, 3 or 4), a group $R^xR^yN(CH_2)_p-$ or $R^xR^yN(CH_2)_pO-$ (wherein p is 1, 2, 3 or 4); wherein when the
5 substituent is $R^xR^yN(CH_2)_p-$ or $R^xR^yN(CH_2)_pO$, R^x with at least one CH_2 of the $(CH_2)_p$ portion of the group may also form a carbocyclyl or heterocyclyl group and R^y may be hydrogen, alkyl.

The word "substantially" does not exclude
10 "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.

Unless specified otherwise, the terms "comprising"
15 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
20 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
25 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
30 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.

Detailed Disclosure of Embodiments

Process for producing metal-containing particles

Generally, the metal-containing particles of the present disclosure are produced by forming a reaction mixture that comprises a metal salt and a reaction medium comprising a capping agent. Upon subjecting the reaction mixture to heat conditions that enable the formation of elemental metal, the elemental metal is formed, thereby forming the metal-containing particle.

Advantageously, the capping agent may also function as a reducing agent. Therefore, the disclosed process may not require the use of other reducing agent(s) such as strong reducing agents, glucose or ascorbic acid, which may be expensive and/or toxic. Therefore, the disclosed process may advantageously be efficient, cost-effective, non-toxic and environmentally friendly.

The process may further advantageously provide surface-coated metal-containing particles that are substantially resistant to oxidation due to at least part of the surface of the metal-containing particle being coordinated to the capping agent, thereby increasing the particle's resistance to oxidation thus maintaining its thermal conductivity when compared to its metallic state.

In a first aspect, there is provided a process for producing metal-containing particles, the process comprising:

- a) forming a reaction mixture comprising (i) a metal salt, and (ii) a reaction medium comprising capping agent, and
- b) subjecting the reaction mixture to conditions to enable formation of elemental metal, thereby forming said metal-containing particles.

Suitable metal salts that may be included in the reaction mixture include any compounds from which elemental metal (metal⁰ or metal having an oxidation state of 0) is formed upon subjecting the reaction mixture to heat conditions.

The metal salt may undergo a disproportionation reaction in which the metal undergoes both reduction and oxidation reactions such that the reduced elemental metal eventually forms. As compared to a sole reduction reaction, by subjecting the metal salt to a disproportionation reaction, the resultant metal may possess a smoother surface, thereby reducing the exposed surface area of the formed elemental-metal containing particle on which oxidation may occur. This may advantageously ensure that the elemental-metal containing particle maintains its thermal conductivity when compared to its metallic state.

The metal salt may be a salt of a transition metal. The transition metal may have a +1 oxidation state. The transition metal may be copper(I) (Cu(I)), silver(I) (Ag(I)), gold(I) (Au(I)) or mercury(I) (Hg(I)).

5 The transition metal may have a +2 oxidation state. The transition metal may be tin(II) (Sn(II)), gallium(II) (Ga(II)), iron(II) (Fe(II)) or cobalt(II) (Co(II)).

The salt may be a nitrate (NO_3^-), sulfate (SO_4^{2-}), halide such as chloride (Cl^-), fluoride (F^-), iodide (I^-)
10 and bromide (Br^-), hydroxide (OH^-), acetate (CH_3COO^-), trifluoroacetate (CF_3COO^-), carbonate (CO_3^{2-}), or acetylacetonate ($\text{C}_5\text{H}_7\text{O}_2^-$).

The metal salt may be a copper(I) salt. The copper(I) salt may undergo disproportionation under
15 suitable conditions to produce elemental copper (Cu^0) that forms a copper particle. The copper particle may be a nanostructure or a microstructure. At least part of the surface of the copper particle may coordinate to the capping agent, thereby increasing the particle's
20 resistance to oxidation thus maintaining its thermal conductivity when compared to its metallic state.

The yield and morphology of the resulting metal-containing particles may be influenced by the initial concentration of the metal salt in reaction mixture, the
25 reaction temperature and/or reaction time.

The initial concentration of the metal salt in the reaction mixture may be in the range of about 0.3 mol/L to about 2.3 mol/L. The initial concentration may be in the range of about 0.5 mol/L to about 2.3 mol/L, about
30 0.7 mol/L to about 2.3 mol/L, about 0.9 mol/L to about 2.3 mol/L, about 1.1 mol/L to about 2.3 mol/L, about 1.3 mol/L to about 2.3 mol/L, about 1.5 mol/L to about 2.3 mol/L, about 1.7 mol/L to about 2.3 mol/L, about 1.9 mol/L to about 2.3 mol/L, about 2.1 mol/L to about 2.3

mol/L, about 0.3 mol/L to about 2.1 mol/L, about 0.3 mol/L to about 1.9 mol/L, about 0.3 mol/L to about 1.7 mol/L, about 0.3 mol/L to about 1.5 mol/L, about 0.3 mol/L to about 1.3 mol/L, about 0.3 mol/L to about 1.1 mol/L, about 0.3 mol/L to about 0.9 mol/L, about 0.3 mol/L to about 0.7 mol/L, about 0.3 mol/L to about 0.5 mol/L, or about 0.3 mol/L, about 0.5 mol/L, about 0.7 mol/L, about 0.9 mol/L, about 1.1 mol/L, about 1.3 mol/L, about 1.5 mol/L, about 1.7 mol/L, about 1.9 mol/L, about 2.1 mol/L, or about 2.3 mol/L. The initial concentration may be in the range of about 1.35 mol/L to about 1.85 mol/L. The initial concentration may be about 1.35 mol/L, about 1.68 mol/L or about 1.85 mol/L.

The metal salt may be copper(I) chloride (CuCl).
The initial concentration of CuCl in the reaction mixture may be in the range of about 0.03 kg/L to about 0.30 kg/L. The initial concentration may be in the range of about 0.06 kg/L to about 0.30 kg/L, about 0.09 kg/L to about 0.30 kg/L, about 0.12 kg/L to about 0.30 kg/L, about 0.15 kg/L to about 0.30 kg/L, about 0.18 kg/L to about 0.30 kg/L, about 0.21 kg/L to about 0.30 kg/L, about 0.24 kg/L to about 0.30 kg/L, about 0.27 kg/L to about 0.30 kg/L, about 0.03 kg/L to about 0.27 kg/L, about 0.03 kg/L to about 0.24 kg/L, about 0.03 kg/L to about 0.21 kg/L, about 0.03 kg/L to about 0.18 kg/L, about 0.03 kg/L to about 0.15 kg/L, about 0.03 kg/L to about 0.12 kg/L, about 0.03 kg/L to about 0.09 kg/L, about 0.03 kg/L to about 0.06 kg/L, or about 0.03 kg/L, about 0.06 kg/L, about 0.09 kg/L, about 0.12 kg/L, about 0.15 kg/L, about 0.18 kg/L, about 0.21 kg/L, about 0.24 kg/L, about 0.27 kg/L, or about 0.30 kg/L. The initial amount of CuCl in reaction mixture may be in the range of about 0.13 kg/L to about 0.19 kg/L. The initial amount of

CuCl in reaction mixture may be about 0.13 kg/L, about 0.17 kg/L or about 0.18 kg/L.

The reaction may take place at a temperature of at least 180 °C, or in the range of about 180 °C to about 5 300 °C. In some embodiments, the reaction may take place at a temperature range from about 190 °C to about 300 °C, about 200 °C to about 300 °C, about 210 °C to about 300 °C, about 220 °C to about 300 °C, about 230 °C to about 300 °C, about 240 °C to about 300 °C, about 250 °C to 10 about 300 °C, about 260 °C to about 300 °C, about 270 °C to about 300 °C, about 280 °C to about 300 °C, about 290 °C to about 300 °C, about 180 °C to about 290 °C, about 180 °C to about 280 °C, about 180 °C to about 270 °C, about 180 °C to about 260 °C, about 180 °C to about 250 15 °C, about 180 °C to about 240 °C, about 180 °C to about 230 °C, about 180 °C to about 220 °C, about 180 °C to about 210 °C, or about 180 °C to about 200 °C. In some embodiments, the reaction may take place at a temperature of about 180 °C, about 190 °C, about 200 °C, about 210 20 °C, about 220 °C, about 230 °C, about 240 °C, about 250 °C, about 260 °C, about 270 °C, about 280 °C, about 290 °C, or about 300 °C. The reaction temperature may be about 270 °C.

The temperature of the reaction may affect the speed 25 of nucleation and growth of elemental metal-containing particles from metal salt. Generally, a higher temperature may increase the speed of initial nucleation. This may produce uniform metal-containing nanowires. A lower temperature may result in slower initial nucleation 30 resulting in non-uniform metal-containing nanowires with smaller metal-containing nanoparticles.

The reaction medium may consist essentially of capping agent. The reaction medium may consist of capping agent. As used in this context, the term "consist

essentially of" refers to the reaction medium consisting of capping agent but for the presence of any impurities.

The reaction time may be varied and depends upon the quantities of materials which are reacted together and upon the reaction temperatures used. The reaction time may be in the range of about 1 minute to about 2.0 hours, or about 5 minutes to about 2.0 hours, about 10 minutes to about 2.0 hours, about 15 minutes to about 2.0 hours, about 30 minutes to about 2.0 hours, about 1.0 hour to about 2.0 hours, about 1.5 hours to about 2.0 hours, about 1 minute to about 1.5 hours, about 1 minute to about 1.0 hour, about 1 minute to about 0.5 hours, about 1 minute to about 15 minutes, about 1 minute to about 10 minutes, about 1 minute to about 5 minutes, or about 1 minute, about 2 minutes, about 5 minutes, about 10 minutes, about 15 minutes, about 30 minutes, about 1.0 hour, about 1.5 hours or about 2.0 hours. The reaction time may be about 1.0 hour. The capping agent may stabilize the resulting metal-containing particles (e.g. by changing the surface energies of different facets) and prevent aggregation between the particles. The capping agent may be incorporated into the matrix during formation of the metal particle-based composite. The capping agent may stabilize the surface of the obtained metal-containing particles and prevent oxidation of their surface when exposed to oxygen and air. The capping agent may also preferentially interact and adhere to a lateral surface of a growth particle, such that the capping agent confines the lateral surface from growing and encourages a cross section surface of the particle to form.

The capping agent may be selected from the group consisting of amines, fatty acids, alkyl thiols, alkyl phosphine oxides, alkyl phosphonic acids, alkyl

phosphines, nitrogen-containing aromatics, and mixtures thereof.

The capping agent may be an amine. The capping agent may be an amine of Formula (I):



wherein:

R^1 is an optionally substituted C_{1-35} alkyl, C_{1-35} alkenyl or C_{1-35} alkynyl; and

R^2 and R^3 are hydrogen, optionally substituted C_{1-35} alkyl, C_{1-35} alkenyl or C_{1-35} alkynyl.

The amine capping agent may be derived from its acid precursor.

The capping agent may be dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, oleylamine, oleic acid, or mixtures thereof. Where the capping agent is oleylamine, it may be derived from its acid precursor, oleic acid, which can be naturally found in various animal and vegetable fats and oils. Therefore advantageously, the disclosed process may be considered to be environmentally friendly as it may involve the use of environmentally benign and renewable sources.

The capping agent may advantageously function as both the reaction medium and coordinating agent to stabilize the surface of the formed metal-containing particles. The capping agent may also preferentially interact and adhere to a lateral surface of a growth particle, such that the capping agent confines the lateral surface from growing and encourages a cross section surface of the nanostructure to form. Therefore this process may be simple, efficient, cost-effective, non-toxic, and environmentally friendly.

The capping agent may also advantageously function as a reducing agent. Advantageously, the disclosed process does not require any other reducing agent(s).

5 In the disclosed process, oxygen may be eliminated from the reaction medium prior to step a) as defined above. Generally, the reaction medium may be heated in an inert atmosphere while being periodically subjected to a degassing process to eliminate air/dissolved oxygen. This may prevent the oxidation of the elemental metal during
10 the reaction.

The metal salt may be introduced to the reaction medium at a temperature of between about 60 °C to about 120 °C. In some embodiments, the temperature may be between about 65 °C to about 120 °C, between about 70 °C
15 to about 120 °C, between about 75 °C to about 120 °C, between about 80 °C to about 120 °C, between about 85 °C to about 120 °C, between about 90 °C to about 120 °C, between about 95 °C to about 120 °C, between about 100 °C to about 120 °C, between about 105 °C to about 120 °C,
20 between about 110 °C to about 120°C, between about 115 °C to about 120°C, between about 60 °C to about 115 °C, between about 60 °C to about 110 °C, between about 60 °C to about 105°C, between about 60 °C to about 100 °C, between about 60 °C to about 95 °C, between about 60 °C
25 to about 90 °C, between about 60 °C to about 85 °C, between about 60 °C to about 80 °C, between about 60 °C to about 75 °C, between about 60 °C to about 70 °C, between about 60 °C to about 65 °C. In some embodiments the temperature is about 60 °C, about 70 °C, about 80 °C,
30 about 90 °C, about 100 °C, about 110 °C, or about 120 °C.

In the disclosed process, the reaction mixture may be subjected to conditions to enable the disproportionation of the metal salt, thereby forming the metal-containing particles (from the elemental metal).

The conditions to enable the disproportionation of the metal salt may comprise heating the reaction mixture.

Upon formation of the reaction mixture, the reaction contents may be heated. Generally, the reaction mixture may be heated to a temperature of at least 180 °C, or in the range of about 180 °C to about 300 °C. In some embodiments, the reaction mixture may be heated to a temperature in the range of about 190 °C to about 300 °C, about 200 °C to about 300 °C, about 210 °C to about 300 °C, about 220 °C to about 300 °C, about 230 °C to about 300 °C, about 240 °C to about 300 °C, about 250 °C to about 300 °C, about 260 °C to about 300 °C, about 270 °C to about 300 °C, about 280 °C to about 300 °C, about 290 °C to about 300 °C, about 180 °C to about 290 °C, about 180 °C to about 280 °C, about 180 °C to about 270 °C, about 180 °C to about 260 °C, about 180 °C to about 250 °C, about 180 °C to about 240 °C, about 180 °C to about 230 °C, about 180 °C to about 220 °C, about 180 °C to about 210 °C, about 180 °C to about 200 °C, or about 180 °C to about 180 °C. In some embodiments, the reaction mixture may be heated to a temperature of about 180 °C, about 190 °C, about 200 °C, about 210 °C, about 220 °C, about 230 °C, about 240 °C, about 250 °C, about 260 °C, about 270 °C, about 280 °C, about 290 °C, or about 300 °C.

Therefore, the disclosed process may advantageously be a convenient one-pot synthesis in which metal-containing particles can be produced via a single step heating process.

The reaction medium comprising the capping agent may be reused. The metal-containing particles may be separated from the reaction medium by filtration or centrifugation, and the reaction medium may be reused for

the synthesis of further metal-containing particles without any pretreatment.

Therefore, the disclosed process may further comprise the following steps:

- 5 c) recycling the reaction medium;
- d) forming a reaction mixture comprising a metal salt and the recycled reaction medium of step c);
- e) subjecting the reaction mixture to heat conditions to enable the formation of elemental metal,
- 10 thereby forming metal-containing particles.

Steps c) to e) may be repeated from one to three times. Therefore, the reaction medium may be reused for two, three or four successive batches. Generally, the used reaction medium may be topped up with a small amount

15 of fresh capping agent to compensate for any lost capping agent during the reaction and product separation steps of the previous batch.

The disclosed metal-containing particles may have nano- or micro-scale dimensions. The disclosed metal-containing particles may be metal-containing nanostructures or microstructures.

20

The disclosed metal-containing nanostructures may comprise a mixture of nanowires, nanorods and/or nanoparticles. The dimension of the nanostructure may refer to the width or diameter (or equivalent diameter), where appropriate and may be equal to or less than 1000 nm, or equal to or less than 100 nm.

25

The disclosed metal-containing particles may comprise a mixture of microwires, microrods and/or microparticles.

30

The disclosed process may also be used together with a further surface protecting agent to protect the surface of the obtained metal-containing particles from long-term oxidation. In this embodiment, a post-treatment step with

a surface protecting agent may be used. Suitable surface protecting agents include tributylphosphine, trioctylphosphine and triphenylphosphine.

Advantageously, high yield metal-containing particles may be obtained by the disclosed process, even after the reaction medium is reused in subsequent batches. Between about 30% to about 50% metal-containing particles may be obtained per batch. In other embodiments, between about 34% to about 50%, between about 38% to about 50%, between about 42% to about 50%, between about 46% to about 50%, between about 30% to about 46%, between about 30% to about 42%, between about 30% to about 38%, or between about 30% to about 34%. In some embodiments, about 30%, about 34%, about 38%, about 42%, about 46%, or about 50% metal-containing particles may be obtained per batch.

The process may further comprise the step of agitating the reaction mixture. The agitation of the reaction mixture may control the growth of the metal-containing particles. Agitating the reaction mixture may comprise stirring the reaction mixture.

Use of disclosed metal-containing particles

The disclosed metal-containing particles may be used to dope phase change materials in order to enhance their thermal conductivity.

In a second aspect, there is provided a process for producing a thermally conductive composition, the process comprising adding a metal-containing particle produced by the process as disclosed above to a heat transfer medium.

The metal-containing particles may be dispersed in the heat transfer medium. Optionally, a small amount of alcohol, such as ethanol, may be used to aid the dispersion.

The amount of alcohol used may be less than about 0.1% to about 2.0%, or less than about 0.5% to about 2.0%, or less than about 1.0% to about 2.0%, or less than about 1.5% to about 2.0%, or less than about 0.1% to about 1.5%, or less than about 0.1% to about 1.0%, or less than about 0.1% to about 0.5% alcohol. The amount of alcohol used may be about 0.1%, or about 0.5%, or about 1.0%, or about 1.5%, or about 2.0% alcohol.

The process may further comprise the step of selecting about 0.02 weight percent (wt%) to about 0.20 wt% metal-containing particle as disclosed above based on the thermally conductive composition. The thermally conductive composition may comprise about 0.04 wt% to about 0.20 wt%, about 0.06 wt% to about 0.20 wt%, about 0.08 wt% to about 0.20 wt%, about 0.10 wt% to about 0.20 wt%, about 0.12 wt% to about 0.20 wt%, about 0.14 wt% to about 0.20 wt%, about 0.16 wt% to about 0.20 wt%, about 0.18 wt% to about 0.20 wt%, about 0.02 wt% to about 0.18 wt%, about 0.02 wt% to about 0.16 wt%, about 0.02 wt% to about 0.14 wt%, about 0.02 wt% to about 0.12 wt%, about 0.02 wt% to about 0.10 wt%, about 0.02 wt% to about 0.08 wt%, about 0.02 wt% to about 0.06 wt%, or about 0.02 wt% to about 0.04 wt% metal-containing particle as disclosed above. The thermally conductive composition may comprise about 0.02 wt%, about 0.04 wt%, about 0.06 wt%, about 0.08 wt%, about 0.10 wt%, about 0.12 wt%, about 0.14 wt%, about 0.16 wt%, about 0.18 wt%, or about 0.20 wt% metal-containing particle as disclosed above.

In a third aspect, there is provided a thermally conductive composition comprising a heat transfer medium and a metal-containing particle produced by the disclosed process.

The thermally conductive composition may comprise about 0.02 weight percent (wt%) to about 0.20 wt% metal-

containing particle as disclosed above based on the thermally conductive composition. The thermally conductive composition may comprise about 0.04 wt% to about 0.20 wt%, about 0.06 wt% to about 0.20 wt%, about 5 0.08 wt% to about 0.20 wt%, about 0.10 wt% to about 0.20 wt%, about 0.12 wt% to about 0.20 wt%, about 0.14 wt% to about 0.20 wt%, about 0.16 wt% to about 0.20 wt%, about 0.18 wt% to about 0.20 wt%, about 0.02 wt% to about 0.18 wt%, about 0.02 wt% to about 0.16 wt%, about 0.02 wt% to 10 about 0.14 wt%, about 0.02 wt% to about 0.12 wt%, about 0.02 wt% to about 0.10 wt%, about 0.02 wt% to about 0.08 wt%, about 0.02 wt% to about 0.06 wt%, or about 0.02 wt% to about 0.04 wt% metal-containing particle as disclosed above. The thermally conductive composition may comprise 15 about 0.02 wt%, about 0.04 wt%, about 0.06 wt%, about 0.08 wt%, about 0.10 wt%, about 0.12 wt%, about 0.14 wt%, about 0.16 wt%, about 0.18 wt%, or about 0.20 wt% metal-containing particle as disclosed above.

The heat transfer medium may refer to any medium 20 capable of transferring heat and includes solid, gaseous and liquid fluids and phase change materials. Phase change materials include, for example, fluids that are gaseous under atmospheric pressure but are liquid or semi-liquid under the ambient operating conditions of the conductivity system, and viscous fluids. Phase change 25 materials are those that change from one phase, such as a solid, to a flowable material, such as a liquid or viscous fluid, at the operating temperature of the composition.

30 The heat transfer medium may be prepared by polymerizing one or more alpha-olefin monomers with one or more vinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers,

and optionally with other polymerizable ethylenically unsaturated monomer(s).

The heat transfer medium may include conjugated polymers, crystalline polymers, amorphous polymers, 5 epoxies, resins, acrylics, polycarbonates, polyphenylene ethers, polyimides, polyesters, acrylonitrile-butadiene-styrene (ABS); polymers such as polyethylene, polypropylene, polyamides, polyesters, polycarbonates, polyphenylene oxide, polyphenylene sulphide, 10 polyetherimide, polyetheretherketone, polyether ketone, polyimides, polyarylates, styrene, poly(tetramethylene oxide), poly(ethylene oxide), poly(butadiene), poly(isoprene), poly(hydrogenated butadiene), poly(hydrogenated isoprene), liquid crystal polymers, 15 polycarbonate, polyamide-imide, copolyimides precursors, reinforced polyimide composites and laminates made from said polyimides, polyphenylated polynuclear aromatic diamines, fluorocarbon polymers, polyetherester elastomers, neoprene, polyurea, polyanhydride 20 chlorosulphonated polyethylene, and ethylene/propylene/diene (EPDM) elastomers, polyvinyl chloride, polyethylene terephthalate, polyvinylchloride, ABS, polystyrene, polymethylmethacrylate, polyurethane and high performance engineering plastics, polyacrylate, 25 polymethacrylate, and polysiloxane, aromatic copolyimide, polyalpholefins, polythiophene, polyaniline, polypyrrole, polyacetylene, polyisocyanurates, their substituted derivatives and similar polymers. Such polymers may contain stabilizers, pigments, fillers and other 30 additives known for use in polymer compositions.

The heat transfer medium may include monomers that further include vinyl monomers such as styrene, vinyl pyridines, N-vinyl pyrrolidone, vinyl acetate, acrylonitrile, methyl vinyl ketone, methyl methacrylate,

methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate; polyols such as ethylene glycol, 1,6-hexane diol, and 1,4-cyclohexanedicarbinol; polyamines such as 1,6-hexadiazine and 4,4'-methylenebis
5 (N-methylaniline); polycarboxylic acids such as adipic acid and phthalic acids; epoxides such as ethylene oxide, propylene oxide, and cyclohexene oxide; and lactams such as epsilon-caprolactam. The heat transfer medium may be poly(alkylene glycols) such as poly(ethylene glycol)
10 (PEG), and poly(propylene glycol) (PPG); vinyl polymers such as poly(styrene), poly(vinyl acetate), poly(vinylpyrrolidone), poly(vinylpyridine), and poly(methyl methacrylate); organic liquid-soluble polysaccharides or functionalized polysaccharides such as
15 cellulose acetate; and crosslinked swellable polysaccharides and functionalized polysaccharides.

The heat transfer medium may be a phase change material.

The phase change material may include salt-hydrates,
20 organic eutectics, clathrate-hydrates, paraffins, hydrocarbons, Fischer-Tropsch hard waxes, and inorganic eutectic mixtures. Examples of these phase change materials include inorganic and organic salts, preferably ammonium and alkali and alkali earth metal salts, such as
25 sulfates, halides, nitrates, hydrides, acetates, acetamides, perborates, phosphates, hydroxides, and carbonates of magnesium, potassium, sodium, and calcium, both hydrated and unhydrated, alone or in combination with these or other media components. Examples of these
30 include potassium sulfate, potassium chloride, sodium sulfate, sodium chloride, sodium metaborate, sodium acetate, disodium hydrogen phosphate dodecahydrate, sodium hydroxide, sodium carbonate decahydrate, hydrated disodium phosphate, ammonium chloride, magnesium

chloride, calcium chloride, calcium bromide hexahydrate, perlite embedded with hydrogenated calcium chloride, lithium hydride, and lithium nitrate trihydrate. Other suitable phase change media include acetamide, methyl fumarate, myristic acid, Glauber's salt, paraffin wax, fatty acids, methyl-esters, methyl palmitate, methyl stearate, mixtures of short-chain acids, capric and lauric acid, commercial coconut fatty acids, propane and methane and the like. The phase change material may be $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

The metal-containing particles such as, for example, copper nanostructures can be effectively applied as a potential phase change material dopant with a variety of potential uses, for example, in phase change materials for window blinds, plaster walls, drywall partitions, gypsum wall boards, ceiling boards, floor boards or embedded concrete for cooling the indoor room temperature in glazed buildings.

Brief Description Of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. 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 is a schematic diagram showing an overall procedure (100) for synthesis of copper nanostructures, including the reusability of the reaction medium.

Fig. 2 is a graph showing the percentage yields of copper nanostructures produced from reused reaction medium for four successive batches.

Fig. 3 is a series of transmission electron microscope (TEM) images at a scale of 1 μm showing the morphology of copper nanostructures produced from the reused reaction medium for four successive batches.

5 Fig. 4 is a graph showing the thermal conductivity enhancement of a hydrated salt phase change material as a function of added copper nanostructure content.

Fig. 5 is a series of comparative TEM images and X-ray diffraction (XRD) patterns of copper nanostructures synthesized at 200 $^{\circ}\text{C}$ versus copper nanostructures
10 synthesized at 270 $^{\circ}\text{C}$. Scale of TEM images: (a) 0.2 μm ; (b) 1 μm ; and (c) 1 μm .

Fig. 6 is a graph showing the yield of copper nanostructures synthesized at 270 $^{\circ}\text{C}$ using increasing
15 amounts of CuCl precursor in oleylamine reaction medium.

Fig. 7a is a fourier transform infrared (FTIR) spectrum of oleylamine (i) before and (ii) after 1 hour of reaction at 270 $^{\circ}\text{C}$ using 4.8 g CuCl in 36 mL medium.

Fig. 7b is a magnified region of the spectra of Fig.
20 7a in the wavenumber range of 1750-1500 cm^{-1} .

Fig. 7c is a magnified region of the spectra of Fig. 7a in the wavenumber range of 2300-1800 cm^{-1} .

Fig. 8 is FTIR spectrum of copper nanostructures obtained after 1 hour of reaction at 270 $^{\circ}\text{C}$ using 4.8 g
25 CuCl in 36 mL medium.

Fig. 9 is a schematic diagram showing the formation of surface-coated copper nanostructures using oleylamine reaction medium with the simultaneous transformation of oleylamine to its corresponding imine and nitrile products ($-R = -C_{17}H_{33}$).

Examples

Non-limiting examples of the invention 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.

Experimental

Chemicals

Copper(I) chloride ($CuCl$, 99%, Sigma-Aldrich), oleylamine ($C_{18}H_{35}NH_2$, 70%, Sigma-Aldrich), hexane (Primechem Chemicals), and hydrated $CaCl_2 \cdot 6H_2O$ salt phase change material (save[®] HS 29, Pluss Polymers) were used as received without further purification.

Example 1: General reaction of disproportionation of Cu^+ precursor to copper nanostructures



Disproportionation of $CuCl$ in oleylamine as a reaction medium, i.e., the transformation of monovalent copper ions (Cu^+) to metallic copper (Cu^0) and divalent copper ions (Cu^{2+}), is used for the synthesis of the copper nanostructures, as shown above.

Example 2: Preparation of oxygen-free reaction medium

Oleylamine (36 ml) was mechanically stirred and heated to 80 °C under argon atmosphere in a round bottom flask while being periodically subjected to a degassing

process using a vacuum pump to eliminate all air/dissolved oxygen.

Example 3: Preparation of copper nanostructures

5 The copper nanostructures comprising a mixture of nanowires, nanorods, and nanoparticles were synthesized via a facile single-step heating process in an oleylamine reaction medium without using any other weak/strong reducing agents.

10 Referring to Fig. 1, a pre-determined amount of copper (I) chloride (2) (1.2 g) was introduced to the oxygen-free oleylamine (4) of Example 2 at a temperature of 80 °C. The reaction mixture was subsequently rapidly heated to 270 °C in single step, during which the copper
15 (I) chloride was completely reacted with oleylamine at around 140-150 °C, as observed by a color change from colorless to yellowish. The reaction temperature was maintained at this temperature for 1 hour to produce copper nanostructures (6), as observed by a presence of
20 reddish colloidal suspension. Then, the reaction solution containing copper nanostructures was allowed to naturally cool to room temperature.

The copper nanostructures were separated from the reaction medium by centrifugation (not shown in Fig. 1).
25 The reaction medium, i.e. used oleylamine (8), was then reused for the synthesis of copper nanostructures without any pretreatment. The collected copper nanostructures were purified by washing with hexane using a dispersion-separation process for at least three times to remove any
30 excess oleylamine from their surface.

Example 4: Reaction medium reusability tests

For the reusability tests of the reaction medium for four successive batches, the used oleylamine (8) from a

previous batch was topped up with a small amount of fresh oleylamine (4) (4-5 ml) to compensate for any lost oleylamine during the reaction and product separation steps of the previous batch.

5 The oleylamine mixture was then heated to 80 °C under argon atmosphere with periodical vacuum degassing. Afterward, the desired amount of copper (I) chloride (2) was added to the oleylamine mixture. The amounts of copper (I) chloride used for the second, third, and
10 fourth batches were 2.4, 3.6, and 4.8 g, respectively. The remaining steps of reaction, product separation, and product purification are the same as mentioned in Example 3.

It was observed that copper nanowires and nanorods
15 were produced in batches 1-3 (nanowires: 50-300 nm in diameter and 2-15 μ m in length; nanorods: 200-700 nm in diameter and 0.5-3 μ m in length).

It was observed that aggregated small nanoparticles and small nanorods were formed in batch 4 (nanoparticles:
20 30-50 nm in diameter; nanorods: 50-80 nm in diameter and 400-700 nm in length).

Example 5: Yield of copper nanostructures from reused reaction medium

25 A high-yield of copper nanostructures can be obtained by this process. Even though the oleylamine reaction medium was reused up to the fourth batch, a high yield of more than approximately 34% per batch could be maintained, as shown in Fig. 2. The morphology of the
30 copper nanostructure products from the four batches are comparatively shown in Fig. 3.

A mixture of nanowires, nanorods, and nanoparticles can be clearly observed. The nanowires and nanorods can still be obtained up to the third batch. It was observed

that after the fourth batch, the viscosity of the oleylamine reaction medium increased. Without wishing to be bound by theory, the increased viscosity may be due to the gradual oxidation-induced degradation of oleylamine molecules with respect to the number of subsequent batches. This may lead to the loss of coordinating ability to effectively stabilize the surface of copper nanostructures for anisotropic growth, resulting in aggregated nanoparticles/nanorods obtained from the fourth batch.

Even though the morphology of copper nanostructure changed upon each reuse of the oleylamine reaction medium, a high yield of copper nanostructures was consistently obtained. By this means, the cost of reaction medium can be reduced, for example, by four times.

Example 6: Thermal conductivity of phase change material doped with copper nanostructures

The synthesized copper nanostructures were tested for their thermal conductivity enhancement of hydrated $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ salt phase change material. The obtained copper nanostructures were easily dispersed in the phase change material with the aid of a small amount of ethanol (i.e. less than 2%). It can be seen from Fig. 4 that the thermal conductivity of the phase change material could be greatly enhanced by doping with only small amounts of the synthesized copper nanostructures, i.e. greater than 50% thermal conductivity enhancement with 0.17 wt% copper doping.

The thermal conductivity enhancement capability of the hydrated $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ salt was tested with different copper contents in the range of 0.02-0.17 wt%. The thermal conductivity results of the phase change material

are represented by its percentage enhancement after copper doping as compared with that of the pure phase change material. As shown in Fig. 4, the thermal conductivity enhancement of the phase change material significantly increased from 0 to ~22%, ~43%, and ~52% with increasing the doping content from 0 to 0.02, 0.08, and 0.17 wt%, respectively. This great thermal conductivity enhancement (~52%), achieved by doping the phase change material with a very small amount of copper (0.17 wt%), demonstrated a high thermal conductivity-enhancing capability of the copper nanostructures synthesized in the present disclosure. The great enhancement with the use of a very small amount of the copper nanostructures makes the doping cost-effective for practical thermal energy storage applications.

When a heat source is supplied at one side of the doped phase change material, the highly thermal conductive copper nanostructures can accumulate heat efficiently so as to heat up their surrounding phase change material rapidly. In comparison, the pure phase change material is heated up very slowly in the absence of copper nanostructures.

Example 7: Yield and morphology of copper nanostructures at different temperatures and amounts of CuCl

The yield and morphology of resulting copper nanostructures may be strongly influenced by the initial amount of CuCl added and reaction temperature (Fig. 5).

Experimentally, 6 mL oleylamine was heated to 80 °C and 0.2 g CuCl was added, followed by heating quickly to 200 °C. After 1 hour of disproportionation of 0.2 g CuCl in 6 mL oleylamine at 200 °C, a lower copper yield of 37% (Fig. 5a) was obtained, in contrast to a maximum copper yield of 50% for complete disproportionation. The copper

product was observed to have a uniform nanowire morphology (~50 nm in diameter and >10 μm in length), revealing one-dimensional anisotropic growth in a controlled manner. The XRD pattern of the copper product
5 (Fig. 5a) shows the face-centered cubic copper phase, as seen from the (111), (200), and (220) crystalline peaks. No copper oxide peaks were observed, revealing the high purity of the copper nanostructures.

To maintain the initial concentration of CuCl at 0.1
10 g per 3 mL medium, both the amount of CuCl and volume of oleylamine were simultaneously increased 6 times to 1.2 g and 36 mL, respectively. For a larger scale synthesis, it was observed that the copper yield was significantly less at 10% after 1 hour of reaction at 200 °C (Fig. 5b),
15 which was lower than 37% for the 0.2 g/6 mL system. The time required to heat the 1.2 g/36 mL system from 80 to 200 °C was ~12 minutes. After maintaining at 200 °C for ~10-15 minutes, reddish colloidal copper was formed. In comparison, it took a shorter amount of time (~6 minutes)
20 to heat the 0.2 g/6 mL system from 80 to 200 °C, and the induction time for the disproportionation of CuCl in oleylamine to form colloidal copper was also much shorter (~1-2 minutes). The faster nucleation and growth of the 0.2 g/6 mL system when compared to the 1.2 g/36 mL
25 system, produced colloidal copper quickly, resulting in uniform copper nanowires. For the 1.2 g/36 mL system, initial nucleation was slower when the temperature increased to 200 °C. Due to its slow disproportionation, even after a certain period of reaction time, the
30 concentration of CuCl precursor was still high enough for slower nucleation to continuously take place, resulting in non-uniform copper nanowires accompanied by smaller nanoparticles (Fig. 5b). As a consequence, the slower nucleation and growth led to the production of copper

nanostructures with a lower yield. The resulting copper nanostructures from this system also have high purity, as revealed by the XRD pattern in Fig. 5b.

To accelerate the disproportionation of CuCl for the
5 1.2 g/36 mL system, the reaction temperature was increased from 200 to 270 °C. As a result, the copper yield greatly increased three-fold to 34% after 1 hour of reaction (Fig. 5c), showing the quicker formation of copper at the elevated temperature. Experimentally,
10 colloidal copper was formed obviously once the temperature reached ~210 °C (~10-15 minutes induction time was observed above, at 200 °C, for the obvious formation of copper). It took another ~5 minutes to increase the temperature up to 270 °C. The faster
15 disproportionation of CuCl at 270 °C quickly produced a higher concentration of Cu⁰ in the reaction system to form much thicker copper nanorods (Fig. 5c), which were achieved by not only the anisotropic growth of copper nanostructures but also the perpendicular growth for
20 thickening them. The fast disproportionation of CuCl did not affect the formation of the pure copper product, as observed from the XRD pattern in Fig. 5c that is similar to the one at 200 °C (Fig. 5b).

For all synthesis conditions, the initial
25 concentration of CuCl precursor and reaction time were kept constant at 0.1 g per 3 mL medium and 1 hour, respectively.

**Example 8: Yield of copper nanostructures synthesized at
30 270 °C using increasing initial amounts of CuCl**

To improve and maximize the copper yield at 270 °C, the initial amount of CuCl added to a controlled volume (36 mL) of the reaction medium was systematically increased from 1.2 g (Fig. 5c) to 2.4, 3.6, 4.2, and 4.8

g. After 1 hour of reaction, the corresponding yield increased proportionally from 34% to 38%, 47%, 49%, and 50%, respectively (Fig. 6). It was observed that a maximum yield of 50% was achieved with the use of 4.8 g CuCl. With further increase in the initial amount of CuCl to 6.0 and 6.6 g, the maximum yield was retained. After the initial amount was continuously increased to 7.2, 7.7, and 8.0 g, lower copper yields of 48%, 48%, and 46%, respectively, were achieved after 1 hour of reaction, slightly less than 50%. When the initial amount of CuCl precursor was further increased, the copper yield was continuously decreased due to the presence of more insoluble precursor at the reaction temperature for the formation of copper nanostructures. The results revealed that the optimized range for the initial amount of CuCl, 4.8-6.6 g in 36 mL medium, led to complete disproportionation in 1 hour, providing the maximum copper yield at 270 °C. In comparison, there was an increase in copper yield of ~147% when increasing the amount of CuCl from 1.2 g in 36 mL to 4.8-6.6 g in 36 mL.

With the increase in CuCl concentration from 1.2 to 4.8 g in 36 mL oleylamine, the obvious formation of copper nanostructures was observed at a lower temperature. For the 1.2 g/36 mL system, the color of the yellow reaction solution remained unchanged until the temperature went up to ~210 °C. Beyond that, the solution became darker, indicating the formation of copper nanostructures. For the 4.8 g/36 mL system, the yellow reaction solution became darker quickly after the temperature reached ~190 °C, indicating the faster nucleation to produce more nuclei for the growth of copper nanostructures with the consumption of more CuCl. It is seen that the formation of copper was much faster for the 4.8 g/36 mL system than the 1.2 g/36 mL system at

a lower temperature. Also, the use of more CuCl precursor (4.8–6.6 g in 36 mL) can drive the disproportionation reaction ($\text{Cu}^+ \rightarrow \text{Cu}^0 + \text{Cu}^{2+}$) in the right direction so as to achieve a faster and more complete reaction, leading to an increased copper yield after 1 hour of reaction. For 7.2 and 7.7 g in 36 mL, the fast formation of copper was also observed at a relatively low temperature (~180–185 °C). With these nearly saturated and saturated concentrations, a slightly decreased yield after 1 hour of reaction may arise from a slower diffusion rate in a more viscous system and the co-existence of some insoluble precursor. With prolonging the reaction time, the copper yield was increased. With the change of the initial amount of CuCl added, the copper yield varied drastically but the products were observed to retain a similar morphology. Upon comparing the 0.2 g/6 mL system (Fig. 5a) to the 7.7 g/36 mL system, the synthesis was scaled up by >38 times based on the amount of CuCl used. The results have demonstrated that this synthetic process is scalable with high yields.

Example 9: Mechanism for production of copper nanostructures

To investigate the mechanism for the production of the copper nanostructures, the FTIR spectra of oleylamine before and after 1 hour of reaction at 270 °C for the 4.8 g/36 mL system were recorded and are depicted for comparison in Fig. 7a. The fresh oleylamine showed peaks at 722 cm^{-1} for the $(-\text{C}-\text{C}-)_n$ ($n \geq 4$) bending band, 966 and 1070 cm^{-1} for the $=\text{C}-\text{H}$ bending band, 1465 cm^{-1} for the $-\text{C}-\text{H}$ bending band, 1580 cm^{-1} for the $-\text{N}-\text{H}$ bending band, 2854 and 2924 cm^{-1} for the methyl $-\text{C}-\text{H}$ stretching band, 3005 cm^{-1} for the $\text{C}=\text{H}$ stretching band, and 3300 cm^{-1} for the $-\text{N}-\text{H}$ stretching band. After the reaction and product

separation, the used oleylamine showed decreased intensities for the -N-H stretching and -N-H bending peaks, and two new peaks were observed at 1634 cm^{-1} for the -C=N stretching band and 2028 cm^{-1} for the -C≡N stretching band (Figs. 7b and 7c). These results revealed the transformation of oleylamine ($-\text{CH}_2\text{-NH}_2$) to its corresponding imine ($-\text{CH=NH}$) and ultimately to nitrile ($-\text{C}\equiv\text{N}$) during the synthesis at high temperature. The FTIR spectrum of the resulting copper nanostructures is shown in Fig. 8. The peaks at 3436 and 1636 cm^{-1} are ascribed to -O-H stretching and -O-H bending bands of water adsorbed on the sample. The other peaks corresponding to oleylamine-derived molecules (-N-H bending, -C=N stretching, and -C≡N stretching bands) are also observed, revealing that all of them concurrently exist on the surface of the copper nanostructures.

Based on the experimental results, a schematic diagram for the production of copper nanostructures in oleylamine at $270\text{ }^\circ\text{C}$ is illustrated in Fig. 9. During the process of heating the CuCl/oleylamine mixture to $270\text{ }^\circ\text{C}$, a clear solution forms quickly once the temperature goes up to $\sim 140\text{ }^\circ\text{C}$, indicating the complete formation of the Cu^+ -oleylamine complex. The Cu^+ -oleylamine complex starts disproportionating to form colloidal copper at $\sim 180\text{-}210\text{ }^\circ\text{C}$, depending on the initial concentration of CuCl in the system. At $270\text{ }^\circ\text{C}$, the formation of copper nanostructures was caused by the accelerated disproportionation ($\text{Cu}^+ \rightarrow \text{Cu}^0 + \text{Cu}^{2+}$), resulting in the observed higher yield (Fig. 5c) than the reaction at $200\text{ }^\circ\text{C}$ (Fig. 5b). As observed by the FTIR spectra of the used oleylamine (Fig. 7a), the strong oxidation of oleylamine molecules at $270\text{ }^\circ\text{C}$ produced oleylimine and oleylnitrile molecules, indicating that oleylamine as a reducing agent can also participate in the reduction of Cu^+ to Cu^0 at high

temperature. These three compounds were also observed on the surface of the copper nanostructures (Fig. 8), revealing their surface-coating properties. The surface-coated copper nanostructures have high resistance to oxidation. They possess high stability under ambient conditions, as observed from their luster.

Applications

10 The disclosed metal-containing particles may be used as a potential phase change material dopant to enhance the thermal conductivity of said phase change material.

The doped phase change material may have a variety of potential uses, for example, in phase change materials for window blinds, plaster walls, drywall partitions, gypsum wall boards, ceiling boards, floor boards or embedded concrete for cooling the indoor room temperature in glazed buildings.

20 The disclosed metal-containing particles may be made from a convenient one-pot synthesis comprising a single heating step. The process may therefore be simple and straightforward.

The disclosed process may comprise recycling the reaction medium. The process may therefore be cost-efficient.

The disclosed process may comprise using naturally occurring reaction material. The process may therefore be environmentally friendly and cost-effective.

30 The capping agent may also function as a reducing agent. Therefore, the disclosed process does not involve the use of other reducing agents. As reducing agents may be toxic and expensive, the process may therefore be environmentally friendly and cost-effective.

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
5 the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A process for producing transition metal-containing particles, the process comprising:
 - 5 a) forming a reaction mixture comprising (i) a transition metal salt, and (ii) a reaction medium comprising a capping agent,
 - b) subjecting the reaction mixture to heat conditions to enable the formation of elemental transition
 - 10 metal, thereby forming the transition metal-containing particles, and
 - c) recycling the reaction medium for reuse in step (a).
- 15 2. The process according to claim 1, wherein the capping agent also functions as a reducing agent.
3. The process according to claim 2, wherein the reaction mixture excludes other reducing agent(s).
- 20 4. The process according to any one of claims 1 to 3, further comprising the step of eliminating oxygen from the reaction medium prior to step a).
- 25 5. The process according to any one of claims 1 to 4, further comprising:
 - (d) forming a reaction mixture comprising a transition metal salt and the recycled reaction
 - 30 medium of step c); and
 - (e) subjecting the reaction mixture of step d) to heat conditions to enable the formation of elemental transition metal, thereby forming transition metal-containing particles.
- 35

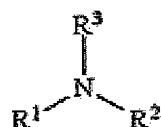
6. The process according to claim 5, wherein steps c) to e) are repeated from one to three times.

7. The process according to any one of claims 1 to 6, wherein step a) and/or step c) is performed at a temperature of between about 60 °C to about 120 °C.

8. The process according to claim 7, wherein step b) and/or step e) comprises heating the reaction mixture to a temperature in the range of about 180 °C to about 300 °C.

9. The process according to any one of claims 1 to 8, wherein the capping agent is selected from the group consisting of amines, fatty acids, alkyl thiols, alkyl phosphine oxides, alkyl phosphonic acids, alkyl phosphines, nitrogen-containing aromatics, and mixtures thereof.

10. The process according to any one of claims 1 to 9, wherein the capping agent is selected from an oleic acid or an amine of Formula (I):



wherein:

R¹ is an optionally substituted C₁₋₃₅ alkyl, C₁₋₃₅ alkenyl or C₁₋₃₅ alkynyl; and
R² and R³ are hydrogen, optionally substituted C₁₋₃₅ alkyl, C₁₋₃₅ alkenyl or C₁₋₃₅ alkynyl.

11. The process according to claim 10, further comprising the step of deriving the amine capping agent from its acid precursor.

12. The process according to any one of claims 1 to 10, wherein the amine is selected from the group consisting of dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, oleylamine, and mixtures thereof.
13. The process according to any one of claims 1 to 12, wherein the transition metal salt is a salt of a transition metal with +1 oxidation state.
14. The process according to claim 13, wherein the transition metal is selected from the group consisting of Cu(I), Ag(I), Au(I) and Hg(I).
15. The process according to any one of claims 1 to 12, wherein the transition metal salt is a salt of a transition metal with +2 oxidation state.
16. The process according to claim 15, wherein the transition metal is selected from the group consisting of Sn(II), Ga(II), Fe(II) and Co(II).
17. The process according to any one of claims 1 to 16, wherein the anion of the transition metal salt is selected from the group consisting of nitrate, sulfate, hydroxide, acetate, trifluoroacetate, carbonate and acetylacetonate.
18. The process according to any one of claims 1 to 17, wherein the transition metal-containing particles have nano- or micro-scale dimensions.
19. The process according to any one of claims 1 to 18, wherein a yield of more than 30% transition metal-containing particles is obtained.

20. The process according to any one of claims 1 to 19,
further comprising the step of coordinating at least part
5 of the surface of the transition metal salt to the
capping agent.
21. The process according to any one of claims 1 to 20,
further comprising the step of agitating the reaction
mixture.
- 10 22. A process for producing a thermally conductive
composition, the process comprising:
a) forming a reaction mixture comprising (i) a transition
metal salt, and (ii) a reaction medium comprising a
capping agent,
15 b) subjecting the reaction mixture to heat conditions to
enable the formation of elemental transition metal,
thereby forming transition metal-containing particles,
c) recycling the reaction medium for reuse in step (a),
and
20 d) adding the transition metal-containing particles
produced by the process of steps (a) to (c) to a heat
transfer medium.
23. The process according to claim 22, wherein the heat
25 transfer medium is a phase change material.
24. The process according to claim 23, wherein the
phase change material is selected from the group
consisting of sodium sulfate, magnesium sulfate, calcium
chloride, magnesium chloride, potassium fluoride,
30 potassium aluminum sulfate, calcium nitrate, magnesium
nitrate, and hydrated salts thereof.
25. The process according to any one of claims 22 to 24,
further comprising the step of selecting 0.02 wt% to 0.20
wt% transition metal-containing particles based on the
35 thermally conductive composition.
26. A thermally conductive composition comprising a heat
transfer medium and a transition metal-containing
particle

produced by the process according to any one of claims 1 to 21.

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27. The composition according to claim 26 wherein the heat transfer medium is a phase change material.

10 28. The composition according to claim 27, wherein the phase change material is selected from the group consisting of sodium sulfate, magnesium sulfate, calcium chloride, magnesium chloride, potassium fluoride, potassium aluminum sulfate, calcium nitrate, magnesium nitrate, and hydrated salts
15 thereof.

29. The composition according to any one of claims 26 to 28, wherein said composition comprises 0.02 wt% to 0.20 wt% transition metal-containing
20 particles based on the thermally conductive composition.