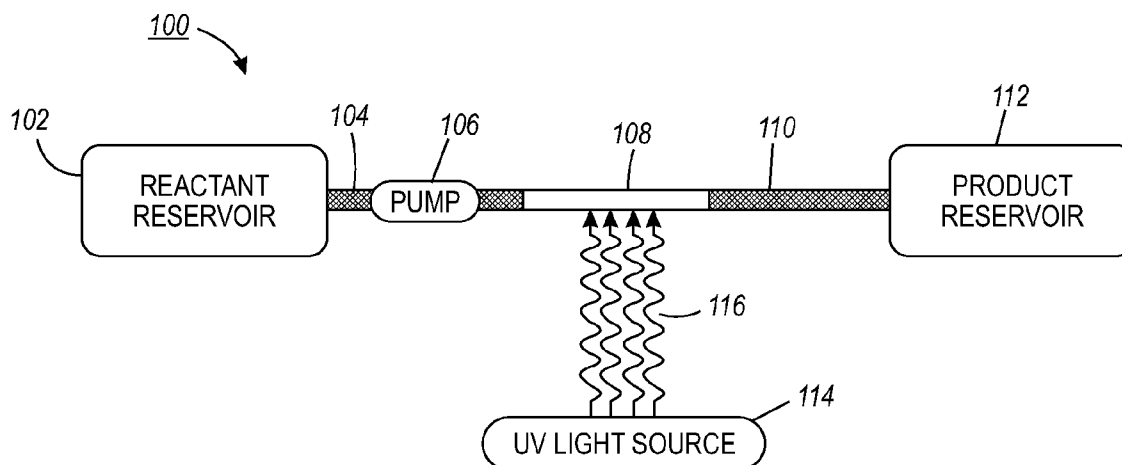




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(19) **United States**(12) **Patent Application Publication**
Enright et al.(10) **Pub. No.: US 2011/0048171 A1**(43) **Pub. Date: Mar. 3, 2011**(54) **CONTINUOUS REACTION PROCESS FOR
PREPARING METALLIC NANOPARTICLES**(75) Inventors: **Thomas E. Enright**, Tottenham
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Mississauga (CA)(73) Assignee: **Xerox Corporation**, Norwalk, CT
(US)(21) Appl. No.: **12/550,219**(22) Filed: **Aug. 28, 2009****Publication Classification**(51) **Int. Cl.**
B22F 9/16 (2006.01)(52) **U.S. Cl.** **75/345; 425/6**(57) **ABSTRACT**

A method for producing metallic nanoparticles in a continuous flow-through reactor comprising combining at least one metallic precursor and at least one radical precursor in a reactant reservoir to form a reactant stream; flowing the reactant stream through at least one channel having a first channel end connected to the reactant reservoir, a second channel end connected to a product reservoir, and at least one clear channel section, which is transparent to activating radiation used to generate a radical reducing agent from the radical precursor, for exposing the reactant stream to a radiation source; exposing the reactant stream in the clear channel section to the radiation source to generate the radical reducing agent, initiate a reaction, and form a product stream comprising metallic nanoparticles; and optionally, collecting the product stream in the product reservoir.



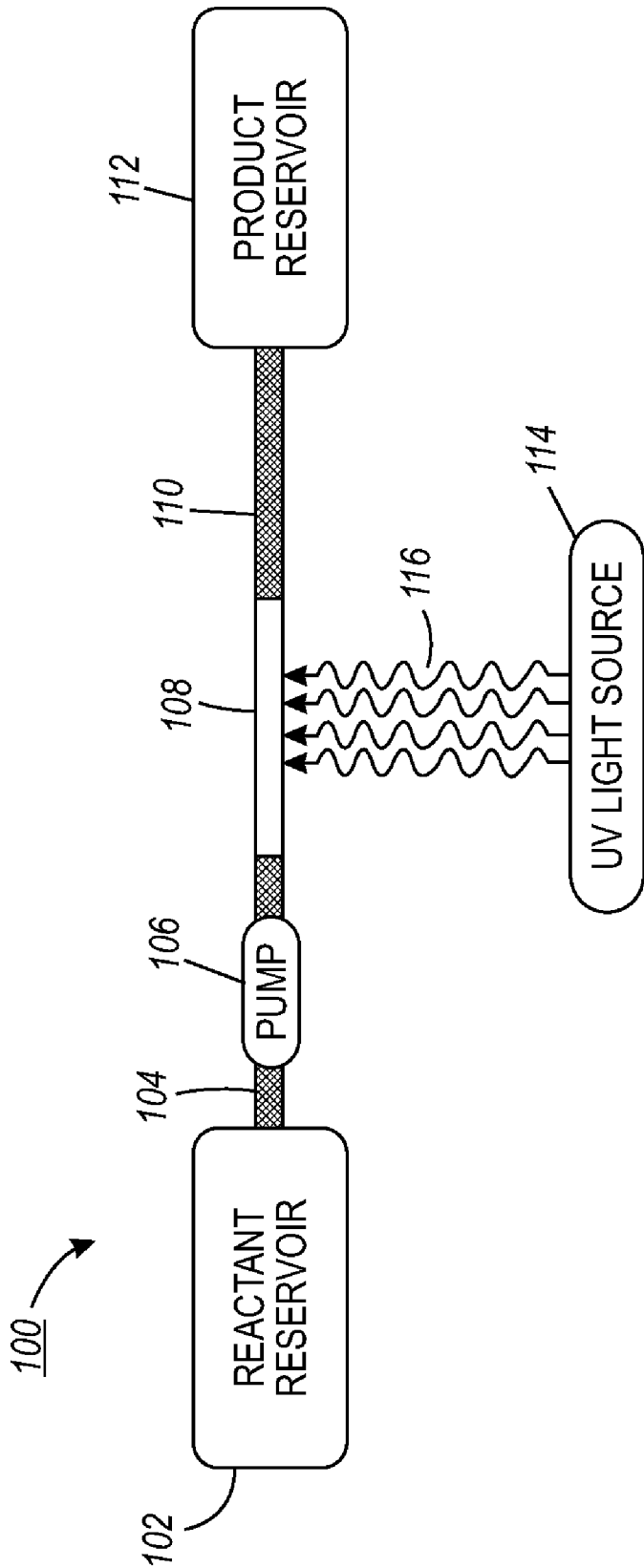


FIG. 1

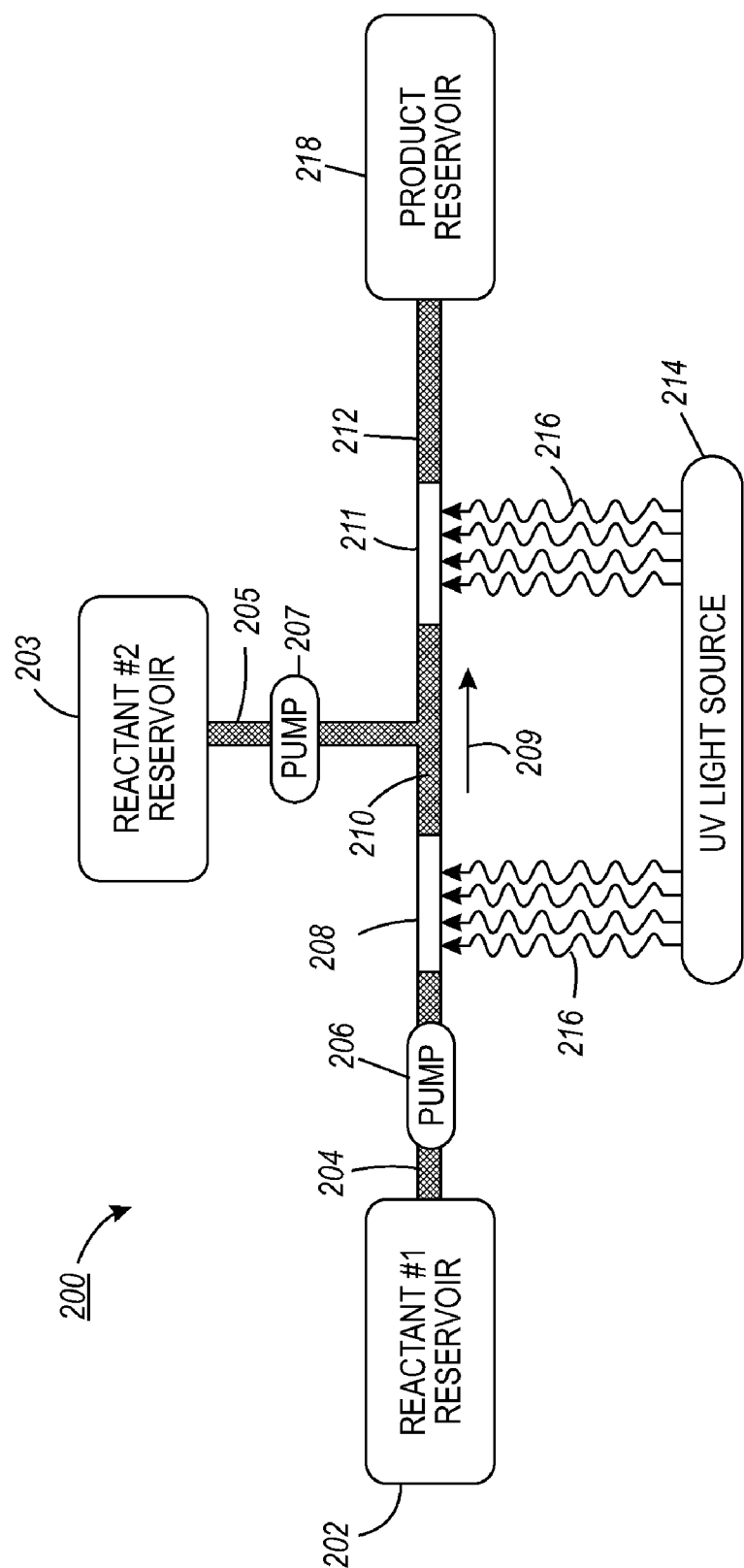


FIG. 2

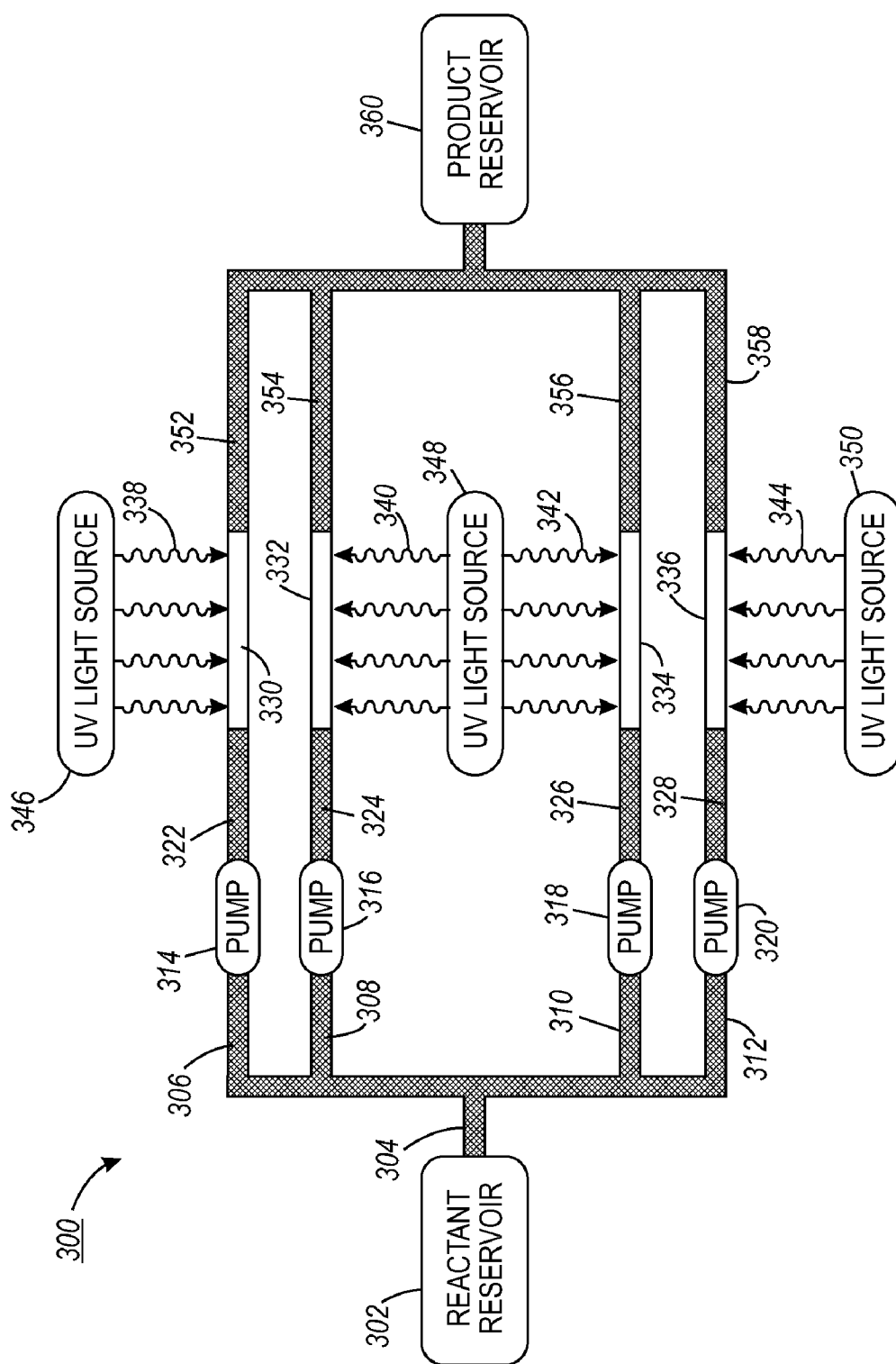


FIG. 3

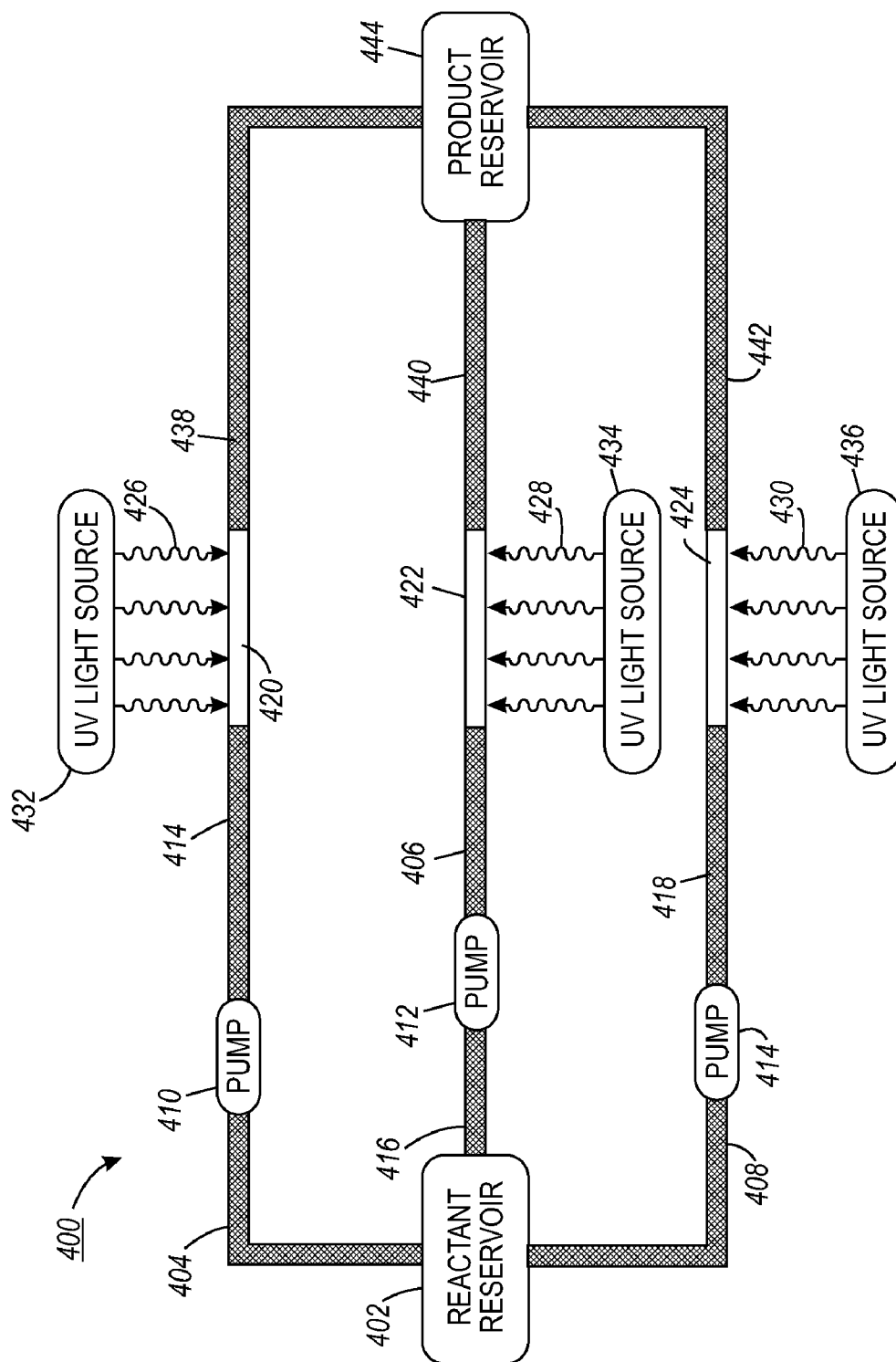


FIG. 4

CONTINUOUS REACTION PROCESS FOR PREPARING METALLIC NANOPARTICLES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] Commonly assigned U.S. patent application Ser. No. 12/126,581, of Michelle Chrétien et al., filed May 23, 2008, entitled "Photochemical Synthesis of Metallic Nanoparticles For Ink Applications," which is hereby incorporated by reference herein in its entirety, discloses a method of forming an ink comprising photochemically producing stabilized metallic nanoparticles and formulating the nanoparticles into an ink.

[0002] Commonly assigned U.S. patent application Ser. No. 12/133,548, of Michelle Chrétien et al., filed Jun. 5, 2008, entitled "Photochemical Synthesis of BiMetallic Core-Shell Nanoparticles," which is hereby incorporated by reference herein in its entirety, discloses a method of photochemically producing bimetallic core-shell nanoparticles, which can be used in ink applications.

TECHNICAL FIELD OF THE DISCLOSURE

[0003] The present disclosure relates to a continuous reaction process for preparing metallic nanoparticles.

BACKGROUND

[0004] Printed electronic features, such as thin film transistor (TFT) electrodes and radio frequency identification (RFID) technology, are an area of intensive research. The ability to directly print electronic features opens the door to a myriad of low-cost flexible electronics with many possibilities for application.

[0005] Materials commonly used for printing electronic features include metal materials. In particular, nanoparticulate metal materials are widely-used in printed electronics applications because they have superior characteristics that yield a better product. Metallic nanoparticles are particles having a diameter in the submicron size range. Nanoparticle metals have unique properties, which differ from those of bulk and atomic species. Metallic nanoparticles are characterized by enhanced reactivity of the surface atoms, high electric conductivity, and unique optical properties. For example, nanoparticles have a lower melting point than bulk metal, and a lower sintering temperature than that of bulk metal. The unique properties of metal nanoparticles result from their distinct electronic structure and from their extremely large surface area and high percentage of surface atoms. Metal nanoparticles, then, can potentially enable production of low cost, flexible electronics. For example, once synthesized and isolated, metal nanoparticles can be dispersed into an ink vehicle, and the ink can be printed on a desired substrate to form an electronic pattern. The metal particles can then be annealed to form a conductive film. The specific metal selected for the nanoparticle can be varied in accordance with the specific application.

[0006] Methods have been proposed for preparing metal particles. For example, metal nanoparticles can be synthesized using a photochemical process. U.S. patent application Ser. No. 12/126,581, which is hereby incorporated by reference herein in its entirety, discloses a method of forming an ink comprising photochemically producing stabilized metallic nanoparticles and formulating the nanoparticles into an ink.

[0007] U.S. patent application Ser. No. 12/133,548, which is hereby incorporated by reference herein in its entirety, discloses a method of photochemically producing bimetallic core-shell nanoparticles, which can be used, for example, in ink applications.

[0008] U. S. Patent Publication 20090142481, which is hereby incorporated by reference herein in its entirety, discloses a low-cost copper nanoparticle ink that can be annealed onto a paper substrate for RFID antenna applications using substituted dithiocarbonates as stabilizers during copper nanoparticle ink production.

[0009] U.S. Pat. No. 7,494,608, which is hereby incorporated by reference herein in its entirety, discloses a composition comprising a liquid and a plurality of silver-containing nanoparticles with a stabilizer, wherein the silver-containing nanoparticles are a product of a reaction of a silver compound with a reducing agent comprising a hydrazine compound in the presence of a thermally removable stabilizer in a reaction mixture comprising the silver compound, the reducing agent, the stabilizer, and an organic solvent wherein the hydrazine compound is a hydrocarbyl hydrazine, a hydrocarbyl hydrazine salt, a hydrazide, a carbazate, a sulfonohydrazide, or a mixture thereof and wherein the stabilizer includes an organoamine. See also U.S. Pat. 7,270,694, which is hereby incorporated by reference herein in its entirety.

[0010] U. S. Patent Publication 20090148600, which is hereby incorporated by reference herein in its entirety, discloses metal nanoparticles with a stabilizer complex of a carboxylic acid-amine on a surface thereof formed by reducing a metal carboxylate in the presence of an organoamine and a reducing agent compound. The metal carboxylate may include a carboxyl group having at least four carbon atoms, and the amine may include an organo group having from 1 to about 20 carbon atoms.

[0011] The appropriate components and process aspects of each of the foregoing U. S. Patents and Patent Publications may be selected for the present disclosure in embodiments thereof. Further, throughout this application, various publications, patents, and published patent applications are referred to by an identifying citation. The disclosures of the publications, patents, and published patent applications referenced in this application are hereby incorporated by reference into the present disclosure to more fully describe the state of the art to which this invention pertains.

[0012] Currently available methods for preparing metallic nanoparticles are suitable for their intended purposes. However, a need remains for an improved, reliable, cost-effective system and method suitable for preparing metallic nanoparticles, bimetallic nanoparticles, and the like. Further, a need remains for an improved system and method for preparing metallic nanoparticles that are suitable for printing electronic features such as by incorporation into inks. Further, a need remains for an improved system and method for preparing metallic nanoparticles that are stable under atmospheric conditions, have a small particle size, and where the particles formed are of a size such that they can be annealed at lower temperatures (<200° C.) so that they can be used with substrates such as paper and plastics. Further, a need remains for a system and method for preparing metallic nanoparticles which provides cost-effectiveness and a high throughput yield. Further, a need remains for an improved system and method for preparing metallic nanoparticles in production sized quantities.

SUMMARY

[0013] Described is a method for producing metallic nanoparticles in a continuous flow-through reactor comprising

combining at least one metallic precursor and at least one radical precursor in a reactant reservoir to form a reactant stream; flowing the reactant stream through at least one channel having a first channel end connected to the reactant reservoir, a second channel end connected to a product reservoir, and at least one clear channel section, which is transparent to activating radiation used to generate a radical reducing agent from the radical precursor, for exposing the reactant stream to a radiation source; exposing the reactant stream in the clear channel section to the radiation source to generate the radical reducing agent, initiate a reaction, and form a product stream comprising metallic nanoparticles; and optionally, collecting the product stream in the product reservoir. In embodiments, two or more different metallic precursors can be combined to provide metal alloy nanoparticles.

[0014] Further described is a method for producing bimetallic or alloy nanoparticles in a continuous flow-through reactor comprising combining at least one first metallic precursor and at least one first radical precursor; combining at least one second metallic precursor and at least one radical precursor; wherein the first and second metallic precursors are the same or different; and wherein the first and second radical precursors are the same or different; flowing the first metallic precursor, and first radical precursor, second metallic precursor, and second radical precursor through a first clear channel section of the reactor and exposing the metallic and radical precursors to a radiation source to initiate a reaction and form a product stream comprising metallic or bi-metallic nanoparticles having a core-shell configuration, an alloy configuration, or a combination thereof; and optionally, collecting the product stream in a product reservoir.

[0015] Further described is a continuous flow-through reactor system for producing metallic nanoparticles comprising at least one reactant reservoir for combining at least one metallic precursor and at least one radical precursor in to form a reactant stream; at least one product reservoir; at least one channel having a first end fluidly connected to the reactant reservoir and a second end fluidly connected to the product reservoir for flowing the reactant stream there through, wherein at least one channel has at least one clear channel section which is transparent to activating radiation used to generate a radical reducing agent from the radical precursor; at least one device for causing the reactant stream to flow from the reactant reservoir through the clear channel section to the product reservoir; at least one radiation source capable of exposing the reactant stream passing through the clear section channel.

[0016] Further described is a continuous flow-through reactor system comprising at least one first reactant reservoir for combining at least one first metallic precursor and at least one first radical precursor in to form a first reactant stream; at least one second reactant reservoir for combining at least one second metallic precursor and at least one second radical precursor in to form a second reactant stream; wherein the first and second metallic precursors are the same or different; and wherein the first and second radical precursors are the same or different; at least one first channel having at least one first clear channel section, a first end fluidly connected to the first reactant reservoir, and a second end fluidly connected to the product reservoir, for flowing the first reactant stream through the first clear channel section to expose the first reactant stream to a radiation source to initiate a reaction and form a first product stream comprising metallic nanoparticles; at least one second channel having at least one second

clear section, a first end fluidly connected to the second reactant reservoir, and a second end fluidly connected to the first channel downstream of the first clear channel section, for flowing the second reactant stream and the first product stream through the second clear channel section to produce a second product stream comprising bimetallic nanoparticles having a core-shell configuration, an alloy configuration, or a combination thereof.

[0017] The advantages of the present disclosure are numerous. The metallic, bimetallic, and alloy nanoparticles herein may be annealed at a lower temperature than the large particle conventional annealing temperature. For example, the nanoparticles herein can be annealed at a temperature of from about 80 to about 300, or from about 100 to about 200° C. rather than large particle annealing temperatures of from about 800 to about 1,500° C. Therefore, inks or other materials containing the present nanoparticles can be printed on a wide variety of substrates, including paper and plastic substrates. The method is also fast, and thus large quantities of nanoparticles can be produced rapidly, in a matter of seconds to a few minutes. The method is also versatile. Bare, unprotected nanoparticles are produced, and the nanoparticles can be stabilized with virtually any molecule by extracting the nanoparticles into an organic solvent containing a stabilizer of choice. Additionally, there are numerous combinations of metals and reducing radical pairs that may be used in this method. For instance, copper can be used in this method. Therefore, this method offers a cheaper alternative to synthesis of metallic nanoparticles using more expensive metals, such as platinum, gold or silver. The size and/or concentration of the nanoparticles can be easily controlled by changing one or more of the parameters of this method, such as irradiation time, irradiation intensity, the metal counter-ion used, and/or the concentrations of the metal or the photoinitiator. Further, the method is ecologically-friendly because it does not require harsh reducing agents, and can be performed at room temperature in water.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. 1 is an illustration of a continuous reaction process and system for preparing metallic nanoparticles in accordance with the present disclosure.

[0019] FIG. 2 is an illustration of a continuous reaction process and system for preparing bimetallic nanoparticles in accordance with the present disclosure.

[0020] FIG. 3 is an illustration of an alternate continuous reaction process and system for preparing metallic nanoparticles in accordance with the present disclosure.

[0021] FIG. 4 is an illustration of another continuous reaction process and system for preparing metallic nanoparticles in accordance with the present disclosure.

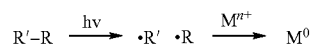
DETAILED DESCRIPTION

[0022] Disclosed is a method comprising using a continuous flow-through reactor for a mono, bimetallic or metal alloy nanoparticle synthesis reaction. The reactants flow through a tubular reactor of which a clear section of the tube is exposed with radiation such as ultra-violet or visible light to initiate the photochemical reaction. The small cross-section of the reactor tube ensures that a maximum amount of the reactants are exposed to the UV light, thus maximizing the reaction efficiency. The reactor and method can be readily scaled up. In embodiments, a large reservoir of reactants can be directed

into multiple tubes, branched tubes, and the like. In embodiments, uni-metallic, bi-metallic or alloy nanoparticles can be prepared in a single tubular reactor or in a series of branched tubular reactors. In one embodiment, at least one channel comprises a single channel having a plurality of branches extending therefrom, and wherein each branch has at least one clear channel section. In another embodiment, at least one channel comprises a plurality of channels, each channel having at least a first channel end connected to the reactant reservoir, a second channel end connected to the product reservoir, and at least one clear channel section for exposing the reactant stream to a radiation source.

[0023] In embodiments, the metallic nanoparticles are gold, silver, copper, platinum, palladium, nickel, lead, rhodium, or combinations thereof. In a specific embodiment, the metallic nanoparticles comprise copper alone or as part of a bimetallic nanoparticle system.

[0024] Generally, metallic nanoparticles may be produced in an aqueous solution by reduction of one or more metallic ions with at least one reducing agent provided as an aqueous solution of reducing agent precursor and metallic salt. The aqueous solution may be de-aerated. The metal nanoparticle synthesis reaction may be conducted in aqueous solution by reduction of a metal salt by a photochemically generated reducing species (such as α -hydroxy or α -amino radicals) as follows



[0025] wherein $R'-R$ is a reducing agent precursor;

[0026] $\cdot R'$ and $\cdot R$ are photochemically generated radicals,

[0027] M^{n+} is a metal cation and n is a number; and

[0028] M^0 is a metal atom and ultimately a metal nanoparticle.

[0029] Alternately, the solutions can be non-aqueous, that is, prepared with an organic solvent, provided that the reducing agent and the salt dissolve in the chosen solvent.

[0030] The metallic precursor can comprise one or more metallic salts. Suitable metallic ions provided as metal salts include ions of copper, aluminum, magnesium, manganese, zinc, chromium, lead, cadmium, cobalt, nickel, gold, silver, platinum, tin, palladium, indium, iron, tungsten, molybdenum, ruthenium, bismuth, other suitable metal ions, and mixtures thereof. In specific embodiments, suitable metallic ions include copper, aluminum, magnesium, zinc, chromium, lead, cadmium, cobalt, nickel, gold, silver, platinum, tin, palladium, iron, tungsten, other suitable metal ions, and mixtures thereof. For example, the metal salt can be provided in the form of metal sulfates, metal halides (such as metal chlorides or metal bromides), metal nitrates, metal acetates, metal nitrites, metal oxides, metal carbonates, metal oxalates, metal pyrazolyl borates, metal azides, metal fluoroborates, metal carboxylates, metal halogencarboxylates, metal hydroxycarboxylates, metal aminocarboxylates, metal aromatic and nitro and/or fluoro substituted aromatic carboxylates, metal aromatic and nitro and/or fluoro substituted aromatic carboxylates, metal sulfonates, and the like.

[0031] In one embodiment, the metal ions are provided as copper (II) ions. The copper (II) ions can be incorporated into metal salts such as, for example, copper sulfate, copper chloride, copper nitrate, or copper acetate. Of course, other metals, and other metal salts, can also be used.

[0032] As the reducing agent, one or more photochemically generated radicals may be used. Radical precursors (reducing agent precursors) are activated upon exposure to radiation to produce the radical. The radicals react with one or more metal cations (M^+ , M^{2+} , etc., wherein M represents a suitable metal), to produce M^0 metal atoms and ultimately unprotected metal nanoparticles. Suitable radical reducing agents include, for example, ketyl, α -amino, phosphinoyl, benzoyl, and acyl radicals. The radicals used according to the present disclosure may be provided from any known source, including commercially available sources. In one embodiment, the radicals are produced by Norrish Type I cleavage of α -hydroxy or α -aminoketones. Such radical precursors are commercially available as, for example, Ciba commercial photoinitiators Irgacure® 184, 127, 2959, 369, 379, etc. In another embodiment, the radicals are produced by a Norrish Type II photoinitiation process, in which a photoexcited ketone (such as, for example, benzophenone) abstracts a proton from a proton donor molecule (such as, for example, isopropanol) to generate two ketyl radicals.

[0033] In embodiments, the aqueous solution of metallic nanoparticles and the radical reducing agent are irradiated for from about 5 seconds to about 90 seconds, such as from about 10 to about 45 seconds or from about 15 to about 30 seconds, although not limited. The intensity of irradiation is from about 0.001 W/cm² to about 10 W/cm², such as from about 0.05 W/cm² to about 5 W/cm², or from about 0.1 W/cm² to about 1 W/cm², although not limited. The source of irradiation may generally be any source known in the art, such as, for example, by ultra-violet (UV) or visible radiation or any radiation wherein the radical precursor absorbs the wavelengths of radiation being used. In embodiments, this results in the synthesis of uncoated metallic nanoparticles.

[0034] The metallic nanoparticles produced are desirably in the nanometer size range. For example, in embodiments, the metallic nanoparticles have an average particle size (such as particle diameter or longest dimension) of from about 1 to about 1000 nanometers (nm), such as from about 50 to about 500 nm, or about 100 to about 200 nm, or about 5 to about 400 nm, or about 30 to about 400 nm, or about 2 to about 20 nm. Herein, "average" particle size is typically represented as d_{50} , or defined as the volume median particle size value at the 50th percentile of the particle size distribution, wherein 50% of the particles in the distribution are greater than the d_{50} particle size value, and the other 50% of the particles in the distribution are less than the d_{50} value. Average particle size can be measured by methods that use light scattering technology to infer particle size, such as Dynamic Light Scattering. The particle diameter refers to the length of the pigment particle as derived from images of the particles generated by Transmission Electron Microscopy.

[0035] The size of the nanoparticle formed may be controlled by changing the irradiation time and intensity, the metal counter-ion, modifying the concentration of the metal ion and/or the photoinitiator, or by other means.

[0036] The metallic nanoparticles may be in any shape. Exemplary shapes of the metallic nanoparticles can include, without limitation, needle-shape, granular, globular, spherical, amorphous shapes, and the like.

[0037] Once prepared, the uncoated metallic nanoparticles may be suspended in an aqueous solution. Unprotected, uncoated metallic nanoparticles may be functionalized by any suitable means known in the art. Moreover, the metallic nanoparticles may be stabilized. Stabilization of the particles

may be achieved by adding stabilizing molecules directly to the aqueous solution containing the nanoparticles. Alternatively, the nanoparticles can be extracted into an organic solvent containing the stabilizing molecules. For example, copper nanoparticles may be stabilized with a substituted dithiocarbonate. In another example, silver nanoparticles may be stabilized with organic acids or amines, such as oleic acid or oleylamine. In another example, gold particles capped with alkylthiol can be used. Other suitable stabilizers generally include, without limitation, organic stabilizers. The term "organic" in "organic stabilizer" refers to, for example, the presence of carbon atom(s), but the organic stabilizer may include one or more non-metal heteroatoms such as nitrogen, oxygen, sulfur, silicon, halogen, and the like. Examples of other organic stabilizers may include, for example, thiol and its derivatives, —OC(=S)SH (xanthic acid), dithiocarbonates, polyethylene glycols, polyvinylpyridine, polyninylpyrrolidone, alkyl xanthate, ether alcohol based xanthate, amines, and other organic surfactants. The organic stabilizer may be selected from the group consisting of a thiol such as, for example, butanethiol, pentanethiol, hexanethiol, heptanethiol, octanethiol, decanethiol, and dodecanethiol; a dithiol such as, for example, 1,2-ethanedithiol, 1,3-propanedithiol, and 1,4-butanedithiol; or a mixture of a thiol and a dithiol. The organic stabilizer may be selected from the group consisting of a xanthic acid such as, for example, O-methylxanthate, O-ethylxanthate, O-propylxanthic acid, O-butylxanthic acid, O-pentylxanthic acid, O-hexylxanthic acid, O-heptylxanthic acid, O-octylxanthic acid, O-nonylxanthic acid, O-decylxanthic acid, O-undecylxanthic acid, O-dodecylxanthic acid and combinations thereof.

[0038] Bi-metallic nanoparticles can be formed by forming core particles and forming a shell over the core particles to provide the bi-metallic core-shell nanoparticles.

[0039] The material that forms the shell can be any suitable metal that will provide the desired properties, such as conductivity and the like. The materials used to form the shell can be the same or different from the materials used to form the core. Suitable shell materials include copper, aluminum, magnesium, manganese, zinc, chromium, lead, cadmium, cobalt, nickel, gold, silver, platinum, tin, palladium, indium, iron, tungsten, molybdenum, ruthenium, bismuth, or other suitable elemental metals and mixtures and alloys thereof. In specific embodiments, suitable shell materials include copper, aluminum, magnesium, zinc, chromium, lead, cadmium, cobalt, nickel, gold, silver, platinum, tin, palladium, iron, tungsten, other suitable shell materials, and mixtures thereof.

[0040] In some embodiments, the core and shell metals are different. For example, copper can be used as a core material in view of its low cost, while precious metals can be used as a shell material in view of their stability to oxygen and high conductivity properties. Such combinations allow for core-shell nanoparticles that can be produced at low cost but with desirable properties.

[0041] In embodiments, the uncoated or functionalized metallic or bimetallic nanoparticles are dispersed in the appropriate vehicle for formulation into an ink.

[0042] FIG. 1 illustrates an embodiment of the present method and system **100** for producing metallic nanoparticles in a continuous flow-through reactor. System **100** includes a reactant reservoir **102** for combining at least one metallic precursor and at least one reducing agent to form a reactant stream **104** comprising an aqueous solution of radical precursor (reducing agent) and metallic salt. A device such as a

pump **106** is provided for flowing the reactant stream **104** through the at least one channel having at least one clear channel section **108** that is transparent to the activating radiation used. Alternately, the systems and processes herein can be configured such that gravity enables the stream or streams to flow there through in the desired manner. The reactant stream **104** is exposed to any suitable irradiation source such as visible light source or a UV light source **114** for exposing the reactant stream to radiation **116** in the clear channel section to initiate a reaction and form a product stream **110** comprising metallic nanoparticles in an aqueous suspension. Optionally, the produced product stream can be collected in the product reservoir **112** where the aqueous suspension of metal nanoparticles can be stored or transferred to another vessel.

[0043] The system and method illustrated in FIG. 1 is shown as a single channel with a single clear channel section. The present disclosure is not limited to this configuration, however. Numerous alternative configurations are contemplated such as, for example, wherein the at least one channel comprises a single channel having a first end fluidly connected to the reactant reservoir **102** and a plurality of branches extending therefrom to form a plurality of reactant stream branches, and wherein each branch has at least one clear channel section. FIG. 2, described further below, illustrates an embodiment for preparing bi-metallic or alloy nanoparticles having a core-shell or alloy configuration. FIG. 3 illustrates one possible embodiment for a branched system and process herein wherein system **300** includes a reactant reservoir **302** having a branched channel **304** extending therefrom including branches **306**, **308**, **310**, and **312** each branch fluidly connected to the reactant reservoir **302**. Devices such as pumps **314**, **316**, **318**, **320** are provided for flowing reactant streams **322**, **324**, **326**, **328** through their respective channels. Branch **306** has a clear channel section **330**. Branch **308** has a clear channel section **332**. Branch **310** has a clear channel section **334**. Branch **312** has a clear channel section **336**. Reactant streams **322**, **324**, **326**, **328** flow through their respective branches to clear channel sections **330**, **332**, **334**, **336** where they are exposed to irradiation **338**, **340**, **342**, **344** from UV light sources **346**, **348**, **350**. UV light source **348** may be configured with multiple lights so as to irradiate clear channels **332**, **334** as illustrated in FIG. 3. Alternately, separate UV light sources can be provided. Reactions are initiated in the clear channel sections **330**, **332**, **334**, **336** and product streams **352**, **354**, **356**, **358**, are formed and collected in product reservoir **360**. Again, numerous variations are contemplated, such as multiple reactant reservoirs containing the same or different reactants, additional branched channels containing one or more clear channel sections, a plurality of radiation sources wherein the reactant stream in each clear channel section is exposed to at least one of the plurality of radiation sources, one or more irradiation sources and types, and one or more collection reservoirs.

[0044] In another embodiment, the at least one channel can include a plurality of individual channels, each channel having at least a first channel end connected to a larger reactant reservoir, or connected to a plurality of individual reactant reservoirs, a second channel end connected to the product reservoir, and at least one clear channel section in each for exposing the reactant stream to a radiation source. FIG. 4 illustrates one possible embodiment wherein system **400** includes a reactant reservoir **402** having a first channel **404**, a second channel **406**, and a third channel **408** extending from

and fluidly connected to the reactant reservoir 402. Devices such as pumps 410, 412, and 414 are provided for flowing reactant streams 414, 416, 418 through their respective channels. First channel 404 has a clear channel section 420. Second channel 406 has a clear channel section 422. Third channel 408 has a clear channel section 424. Reactant streams 414, 415, and 418 flow through their respective channels to clear channel sections 420, 422, 424 are exposed therein to irradiation 426, 428, 430 from UV light sources 432, 434, 436. Reactions are initiated in the clear channel sections 420, 422, 424 and product streams 438, 440, and 442 are formed and collected in product reservoir 444. As described herein, numerous variations are contemplated, such as multiple reactant reservoirs containing the same or different reactants, additional channels containing one or more clear channel sections, one or more irradiation sources and types, and one or more collection reservoirs.

[0045] The process can further include providing a plurality of radiation sources; and exposing the reactant stream in each clear channel section to at least one of the plurality of radiation sources. The plurality of radiation sources can include two or more radiation sources disposed to irradiate one or more of the clear channel sections, wherein the radiation sources are the same or different. Different types of radiation sources can be provided, for example, so that different chemical reactions can be initiated in different channels or branches of the same reaction system and process.

[0046] In embodiments, the channels comprise reactor tubes having small cross-sectional areas such that a maximum amount of the reactants are exposed to the UV light, thus maximizing the reaction efficiency. In embodiments, wherein the clear channel section has a cross-section of from about 1 to about 500 millimeters, or from about 1 to about 10 millimeters, or from about 1 to about 4 millimeters.

[0047] The continuous system herein can easily and inexpensively be upgraded to higher throughput simply by adding more glass tubes into the system, compared to purchasing significantly more expensive bulk reactor equipment.

[0048] In another embodiment, a system and method for producing bimetallic or alloy nanoparticles or a combination thereof in a continuous flow-through reactor is described. In embodiments, the method comprises combining at least one first metallic precursor and at least one first radical precursor in a first reactant reservoir to form a first reactant stream; combining at least one second metallic precursor and at least one second radical precursor in a second reactant reservoir to form a second reactant stream; wherein the first and second metallic precursors are the same or different; and wherein the first and second radical precursors are the same or different; flowing the first reactant stream through a first clear channel section of the reactor which is transparent to activating radiation used to generate a radical reducing agent from the radical precursor to expose the first reactant stream to a radiation source to initiate a reaction and form a first product stream comprising metallic nanoparticles; combining the produced metallic nanoparticles with the second reactant stream downstream of the first clear channel section; flowing the produced metallic nanoparticles and the second reactant stream through a second clear channel section of the reactor that is downstream of the first clear channel section; exposing the produced metallic nanoparticles and the second reactant stream to the radiation source to initiate a reaction and form a second product stream comprising metallic or bi-metallic nanoparticles having a core-shell configuration, an alloy configura-

tion, or a combination thereof; and optionally, collecting the second product stream in a second product reservoir.

[0049] Turning to FIG. 2, a continuous flow-through reactor system and method 200 includes combining at least one first metallic precursor and at least one first reducing agent in a first reactant reservoir 202 to form a first reactant stream 204. A device for flowing the streams such as pump 206 flows the first reactant stream to first clear channel section 208 expose the first reactant stream to radiation source 214 where irradiation 216 initiates a reaction to form a first product stream 210 comprising metallic nanoparticles. At least one second metallic precursor and at least one second reducing agent is combined in a second reactant reservoir 203 to form a second reactant stream 205. A device such as pump 207 can be used to flow second reactant stream 205 through the channels. Second reactant stream 205 is combined with the produced metallic nanoparticles 210 downstream of the first clear channel section 206. The produced metallic nanoparticles 210 and the second reactant stream 205 flow through a second clear channel section 211 of the reactor that is downstream of the first clear channel section 206 where the produced metallic nanoparticles 210 and the second reactant stream 205 are exposed to the radiation source 214 where irradiation 216 initiates a reaction to form a second product stream 212 comprising bimetallic nanoparticles having a core shell or alloy configuration. The second product stream 212 can be collected in product reservoir 218 or disposed in an alternative vessel.

[0050] In embodiments, the first and second metallic precursors can be the same or different, and the first and second reducing agents can be the same or different.

[0051] Alternate embodiments contemplate formation of bimetallic or alloy particles by premixing the two or more different metal salt and radical precursors in the same reservoir and irradiating the mixture simultaneously. For example, the method can comprises premixing the metallic precursors and radical precursors in a single reservoir; and flowing the mixture combined in the single reservoir through at least one clear channel section; exposing the mixture in the clear channel section to the radiation source to initiate a reaction and form a product stream comprising metallic or bimetallic nanoparticles having a core-shell configuration, an alloy configuration, or a combination thereof, and optionally, collecting the product stream in a produce reservoir.

[0052] As with previous embodiments described herein, this embodiment is not limited to a specific configuration, but rather numerous alternative configurations are contemplated such as, for example, wherein the channels comprise two or more branches, wherein each branch can be connected to first, second, third, etc., reactant reservoirs, and wherein each branch has at least one clear channel section or wherein each reactant stream ultimately flows through a branch having a clear channel section that can be treated to initiate a reaction.

[0053] Alternately, a plurality of individual channels can be provided, each channel having a first end connected to at least one reactant reservoir, a second end connected to a product reservoir, and at least one clear channel section in each for exposing the reactant stream to a radiation source.

[0054] Further, a plurality of radiation sources can be provided for exposing the reactant streams in each clear channel section to at least one of the plurality of radiation sources. The plurality of radiation sources can include two or more radiation sources disposed to irradiate one or more of the clear channel sections, wherein the radiation sources are the same

or different. Different types of radiation sources can be provided, for example, so that different chemical reactions can be initiated in different channels or branches of the same reaction system and process.

EXAMPLES

[0055] The following Examples are being submitted to further define various species of the present disclosure. These Examples are intended to be illustrative only and are not intended to limit the scope of the present disclosure. Also, parts and percentages are by weight unless otherwise indicated.

Example 1

[0056] Monometallic copper nanoparticle. With reference to FIG. 1, an aqueous solution containing 0.33 mM of a copper (I or II) salt and 1.0 mM of Irgacure® 2959 (an α -hydroxyketone photoinitiator) is charged into a reactant reservoir, degassed with argon for 5 minutes and then pumped through a tubular reactor as described herein. The feed rate is controlled such that the solution is exposed to UV light in the clear portion of the reactor for a period of 15 to 90 seconds. The resulting slurry that feeds into the product reservoir consists of copper nanoparticles suspended in water. The particle size of nanoparticle ranges from approximately 1 to 1000 nm depending on UV exposure time (longer exposure results in larger particle size).

Example 2

Bimetallic Copper-Silver Nanoparticle

[0057] Part A. With reference to FIG. 2, an aqueous solution containing 0.33 mM of a Cu (I or II) salt and 1.0 mM of Irgacure 2959® (an α -hydroxyketone photoinitiator) is charged into a first reactant reservoir, degassed with argon for 5 minutes, and then pumped through a first section of a tubular reactor as described herein. The feed rate is controlled such that the solution is exposed to UV light for approximately 10 seconds in the first clear section of the reactor. This results in a slurry of Cu nanoparticles suspended in water.

[0058] Part B. An aqueous solution containing 0.33 mM HAuCl_4 and 1 mM Irgacure 2959® is charged into a second reactant reservoir, degassed with argon for 5 minutes, and then pumped into the tubular reactor such that it mixes with the solution prepared in Part A near the outlet of the first clear section of the reactor. This mixed solution is exposed to UV light for 15 to 90 seconds in the second clear section of the reactor. This results in a solution of Cu/Ag nanoparticles. The solution of Cu/Ag nanoparticles can, for example, be collected and re-suspended in a solvent suitable for ink-jet printing.

[0059] It will be appreciated that various of the above-disclosed and other features and functions, or alternatives thereof, may be desirably combined into many other different systems or applications. Also that various presently unforeseen or unanticipated alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art which are also intended to be encompassed by the following claims. Unless specifically recited in a claim, steps or components of claims should not be implied or imported from the specification or any other claims as to any particular order, number, position, size, shape, angle, color, or material.

1. A method for producing metallic nanoparticles in a continuous flow-through reactor comprising:

combining at least one metallic precursor and at least one radical precursor in a reactant reservoir to form a reactant stream;

flowing the reactant stream through at least one channel having a first channel end connected to the reactant reservoir, a second channel end connected to a product reservoir, and at least one clear channel section, which is transparent to activating radiation used to generate a radical reducing agent from the radical precursor, for exposing the reactant stream to a radiation source;

exposing the reactant stream in the clear channel section to the radiation source to generate the radical reducing agent, initiate a reaction, and form a product stream comprising metallic nanoparticles; and

optionally, collecting the product stream in the product reservoir.

2. The method of claim 1, wherein the at least one channel comprises a single channel having a plurality of branches extending therefrom, and wherein each branch has at least one clear channel section; or

wherein the at least one channel comprises a plurality of channels, each channel having at least a first channel end connected to the reactant reservoir, a second channel end connected to the product reservoir, and at least one clear channel section for exposing the reactant stream to a radiation source.

3. The method of claim 1, further comprising: providing a plurality of radiation sources; and exposing the reactant stream in each clear channel section to at least one of the plurality of radiation sources.

4. The method of claim 1, wherein the radiation source is an ultra-violet radiation source, a visible radiation source, or a combination thereof.

5. The method of claim 1, wherein the clear channel section has a cross-section of from about 1 to about 4 millimeters.

6. The method of claim 1, wherein the metallic precursor comprises one or more metallic salts.

7. The method of claim 1, wherein the metallic nanoparticles are gold, silver, copper, platinum, palladium, nickel, lead, or combinations thereof.

8. The method of claim 1, wherein the radical reducing agent is a ketyl radical or an α -amino radical.

9. The method of claim 1, wherein the metallic nanoparticles are from about 5 nanometers to about 400 nanometers in size.

10. A method for producing bimetallic or alloy nanoparticles in a continuous flow-through reactor comprising:

combining at least one first metallic precursor and at least one radical precursor;

combining at least one second metallic precursor and at least one radical precursor;

wherein the first and second metallic precursors are the same or different; and wherein the first and second radical precursors are the same or different;

flowing the first metallic precursor, and first radical precursor, second metallic precursor, and second radical precursor through a first clear channel section of the reactor and exposing the metallic and radical precursors to a radiation source to initiate a reaction and form a product stream comprising metallic or bimetallic nanoparticles having a core-shell configuration, an alloy configuration, or a combination thereof; and

optionally, collecting the product stream in a product reservoir.

11. The method of claim **10**, wherein combining comprises combining at least one first metallic precursor and at least one first radical precursor in a first reactant reservoir to form a first reactant stream;

combining at least one second metallic precursor and at least one second radical precursor in a second reactant reservoir to form a second reactant stream;

wherein the first and second metallic precursors are the same or different; and wherein the first and second radical precursors are the same or different;

flowing the first reactant stream through a first clear channel section of the reactor which is transparent to activating radiation used to generate a radical reducing agent from the radical precursor to expose the first reactant stream to a radiation source to initiate a reaction and form a first product stream comprising metallic nanoparticles;

combining the produced metallic nanoparticles with the second reactant stream downstream of the first clear channel section;

flowing the produced metallic nanoparticles and the second reactant stream through a second clear channel section of the reactor that is downstream of the first clear channel section;

exposing the produced metallic nanoparticles and the second reactant stream to the radiation source to initiate a reaction and form a second product stream comprising metallic or bimetallic nanoparticles having a core-shell configuration, an alloy configuration, or a combination thereof; and

optionally, collecting the second product stream in a second product reservoir.

12. The method of claim **10**, wherein combining comprises premixing the metallic precursors and radical precursors in a single reservoir; and

flowing the mixture combined in the single reservoir through at least one clear channel section;

exposing the mixture in the clear channel section to the radiation source to initiate a reaction and form a product stream comprising metallic or bimetallic nanoparticles having a core-shell configuration, an alloy configuration, or a combination thereof; and

optionally, collecting the product stream in a product reservoir.

13. The method of claim **10**, wherein the radiation source is an ultra-violet radiation source, a visible radiation source, or a combination thereof.

14. The method of claim **10**, wherein the clear channel section has a cross-section of from about 1 to about 4 millimeters.

15. The method of claim **10**, wherein the metallic precursor comprises one or more metallic salts.

16. The method of claim **10**, wherein the metallic nanoparticles are gold, silver, copper, platinum, palladium, nickel, lead, or combinations thereof.

17. The method of claim **10**, wherein the radical is a ketyl radical or an α -amino radical.

18. The method of claim **10**, wherein the metallic nanoparticles are about 5 nanometers to about 400 nanometers in size.

19. A continuous flow-through reactor system for producing metallic nanoparticles comprising:

at least one reactant reservoir for combining at least one metallic precursor and at least one radical precursor in to form a reactant stream;

at least one product reservoir;

at least one channel having a first end fluidly connected to the reactant reservoir and a second end fluidly connected to the product reservoir for flowing the reactant stream there through, wherein the at least one channel has at least one clear channel section which is transparent to activating radiation used to generate a radical reducing agent from the radical precursor;

at least one device for causing the reactant stream to flow from the reactant reservoir through the clear channel section to the product reservoir;

at least one radiation source capable of exposing the reactant stream passing through the clear section channel.

20. The continuous flow-through reactor system of claim **19** comprising:

at least one first reactant reservoir for combining at least one first metallic precursor and at least one first radical precursor in to form a first reactant stream;

at least one second reactant reservoir for combining at least one second metallic precursor and at least one second radical precursor in to form a second reactant stream;

wherein the first and second metallic precursors are the same or different; and wherein the first and second radical precursors are the same or different;

at least one first channel having at least one first clear channel section, a first end fluidly connected to the first reactant reservoir, and a second end fluidly connected to the product reservoir, for flowing the first reactant stream through the first clear channel section to expose the first reactant stream to a radiation source to initiate a reaction and form a first product stream comprising metallic nanoparticles;

at least one second channel having at least one second clear section, a first end fluidly connected to the second reactant reservoir, and a second end fluidly connected to the first channel downstream of the first clear channel section, for flowing the second reactant stream and the first product stream through the second clear channel section to product a second product stream comprising metallic or bimetallic nanoparticles having a core-shell configuration, an alloy configuration, or a combination thereof.

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