

MATRIX ASSISTED INK TRANSPORT

RELATED APPLICATIONS

This application claims priority to US provisional serial no. 60/945,164 filed June 20, 2007, and also to US provisional serial no. 60/929,314 filed June 21, 2007, and also to US provisional serial no. 61/047,642 filed April 24, 2008.

STATEMENT ON FEDERAL FUNDING

The present invention was developed with use of federal funding from NSF- NSEC, Grant No. EEC 0118025; and DARPA-ARD, Grant No. DAAD 19-03-1- 0065; and NSF Grant No. EEC0647560; and ASAF/AFOSR FA9550-08-1-0124. The federal government reserves rights in the invention.

BACKGROUND

Nanoscience focuses on elucidating the unique chemical and physical properties of nanoscale materials that analogous bulk structures do not possess (37, 38). Bottom-up and top-down approaches have been used to synthesize and fabricate such nanoscale materials that are metallic (1, 4, 5, 11), magnetic (6,7), semiconducting (8,9), silica-based (18), and carbon-based, such as fullerenes, and carbon nanotubes, (3, 73) with fine control over particle size and shape (74, 36). In the last decade, nanoscale materials have been studied and characterized using a variety of methods and are becoming better understood.

Nanoscale materials are beginning to be utilized in a growing number of novel applications including applications, that rely mainly on the ability to arrange nano building blocks (NBBs) into

deliberate patterns with controlled feature sizes on surfaces, such as nanocircuit integration (75), biological micro- and nano-array fabrication (76), and nanoscale sensing (77, 78). Current methods for patterning nano building blocks into desired locations usually include the following two steps: 1) a surface pattern-generation step and 2) a nanoparticle self-assembly step. The first step creates pre-patterns on a surface using photolithography, electron beam lithography (EBL), or focused ion beam (FIB) lithography (79), while in the second step, nanoparticles are exposed to and further assembled along the pre-patterned areas on the surface (39). Unfortunately, such surface patterning methods can require expensive instrumentation and may be complicated and time-consuming. For example, avoiding non-specific binding of nanoparticles to unwanted areas during the second step may be often a very difficult, if not impossible task. Such problem can be especially prominent at the sub-100 nm size regime.

Dip-pen nanolithography (DPN) is a single-step direct writing and reading lithography tool utilized for patterning soft inks, such as small organic molecules, DNA, and proteins (60), in some cases, at the millimeter and centimeter scale (61,62). In some cases, it may be more difficult to directly write hard inks, such as nanoparticles, fullerenes, or crystallized conducting polymers, using DPN due to problems with obtaining an even coating of such hard inks on an AFM tip and controlling the ink's transport rate. As the result, the nanoparticle patterns may become inconsistent and have uncontrollable feature sizes. In addition, hard inks may in some cases have a tendency to dry quickly and agglomerate during the DPN process, which makes extended writing times unachievable (63-68).

Thus, a need exists to develop a single step method for direct patterning of hard inks on a surface that will provide a control over the patterned feature size and will allow for longer writing times. In particular, development of direct patterning methods for protein-based nanostructures is important for researchers working in the areas of proteomics and theranostics. Such methods would

allow generating multi- component biological nanostructures of proteins, oligonucleotides and viruses.

US Patent No. 7,005,378 describes patterning of metallic precursors including use of polyethylene oxide to facilitate patterning. The paper "On- Wire Lithography" (Qin et al, Science, vol. 309, July 1, 2005, 113-115) describes preparation of gap structures and filling the gap with a mixture of a conductive polymer and polyethylene oxide. US Patent Publication 2003/0162004 (Mirkin et al., Northwestern University) describes patterning of sol-gel mixtures comprising block copolymers. US Patent Publication 2004/0142106 (Mirkin et al., Northwestern University) describes patterning of precursor magnetic materials. US Patent Publication 2002/0122873 (Mirkin et al., Northwestern University) describes patterning of magnetic nanoparticles using magnetic driving forces. US Patent Publication 2004/0026007 (Hubert et al., MIT) describes deposition of nanoparticles.

SUMMARY

The present application describes among other things methods of making, articles, devices, compositions, and methods of using. One embodiment provides a method comprising: providing a tip, providing an ink disposed at the end of the tip, wherein the ink comprises at least one matrix and at least one nanomaterial different from the matrix, providing a substrate surface, and transporting the ink from the tip to the substrate surface to form a structure on the surface comprising both the matrix and the nanomaterial. In another example, provided is a method comprising: providing a tip, providing an ink disposed at the end of the tip, wherein the ink comprises at least one polymer and at least one nanomaterial, providing a substrate surface, and transporting the ink from the tip to the substrate surface to form a structure on the surface comprising both the polymer and the nanomaterial.

One advantage for at least one embodiment is that it allows forming patterns of inks that may be difficult to pattern. Another advantage for at least one embodiment is that it does not require chemical or physical modification of the tip or stamp. In addition, this in many cases does not require chemical or physical modification of the substrate surface and allows transporting ink molecules to the surface in a fashion that is independent of the substrate surface's material. In many embodiments, the method allows sub-micron and sub 100-nm patterns of hard inks such as nanomaterials and biomolecules such as proteins or peptides in a direct write high-throughput manner.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 schematically illustrates patterning of nanomaterials using matrix assisted Dip-Pen nanolithography (DPN).

FIGURES 2 (A)-(F) present DPN generated patterns of various polymers on a variety of substrates as well as selected height profiles. (A) is a topographic atomic force microscopy (AFM) image of a pattern of polyethylene glycol (PEG) with molecular weight (MW) 8,000 on an Au substrate at writing speed of 0.16 $\mu\text{m/s}$. (B) is an AFM image of a pattern of PEG (MW 8,000) on a GaAs substrate at writing speed of 0.022 $\mu\text{m/s}$. (C) is an AFM image of a pattern of polyethylene oxide (PEO) with MW 100,000 on a SiO_x substrate at writing speed of 0.05 $\mu\text{m/s}$. (D) is an AFM image of a pattern of PEO (MW 100,000) on an Au substrate at writing speed of 0.05 $\mu\text{m/s}$. (E) is an AFM image of a pattern of polyethylene imine (PEI) with MW 10,000 on InAs at 0.6 and 0.3 $\mu\text{m/s}$. (F) is an AFM image of a pattern of a mixture of PEI (MW 10,000) and 2 nm Au nanoparticles on InAs at 0.6 and 0.3 $\mu\text{m/s}$.

FIGURES 3 (A) and 3 (B) present height profiles of line patterns of: (A) PEI only; (corresponding topographic AFM image in FIG. 2E) and (B) a mixture of 2 nm Au nanoparticles and PEI on InAs substrate (corresponding topographic AFM image in FIG. 2F). FIGURE 3(C) is a height

profile of PEO only line patterns on Au (corresponding AFM topographic image was shown in FIG. 2D).

FIGURES 4 (A)-(D) present images DPN generated arrays. (A) is a topographic AFM image of PEO arrays at contact time of 64, 32, and 16 seconds from top to bottom, respectively. (B) shows a topographic AFM image of dot arrays deposited using a mixture 2 nm Au nanoparticles and PEO, tip substrate contact time is 64, 32 and 16 seconds from top to bottom respectively. (C) is a topographic AFM image of dot arrays using deposited using a mixture of 5 nm Au nanoparticles and PEO, tip-substrate contact times 64, 32, 16, and 8 from top to bottom respectively, the inset shows a Transmission Electron Microscopy (TEM) image of the dot created by DPN on a TEM grid. (D) shows a topographic AFM image of dot arrays deposited using a mixture 13 nm Au nanoparticles and PEO, tip substrate contact time is 64, 32 and 16 seconds from top to bottom respectively.

FIGURES 5 (A)-(D) present images of patterns generated by DPN using a mixture of 4.7 nm magnetic nanoparticle and PEO. (A) is an AFM image of dot arrays, tip substrate contact time is 64, 32 and 16 seconds from top to bottom respectively. (B) is an AFM image of diamond shape line arrays, writing speed $0.05 \mu\text{m/s}$. (C) is a magnetic force microscopy (MFM) image of larger scale dot arrays. The inset shows a single dot scan (G) is a MFM image of an array of diamond shaped lines created by DPN. The inset shows a single diamond shape line scan.

FIGURES 6 (A)-(D) relate to arrays generated by DPN using a mixture of fullerene and PEO. (A) is an AFM image of dot arrays at contact times of 16, 8 and 4 seconds from top to bottom respectively. (B) is a height profile of the dot arrays of (A). (B) presents line arrays at writing speed of 0.05, 0.1 and $0.2 \mu\text{m/s}$ respectively. (C) is a 3- dimensional AFM image of DPN generated lines crossing through the 500 nm gap nanoelectrode. (F) shows I- V curves of the lines of (E).

FIGURES 7 (A) and (B) are respectively a topographic AFM image (A) and a height profile (B) of fullerene/PEO dot patterns on Au substrate generated by DPN. Contact times are 64, 32, and 16 sec from top to bottom of FIG. 7A, respectively. FIGURE 7 (C) is a height profile of fullerene/PEO line patterns on Au substrate generated by DPN at writing speeds of 0.05, 0.1, and 0.2 $\mu\text{m/s}$ from left to right, respectively. The corresponding AFM topography image was shown in FIG. 6B.

FIGURE 8 schematically illustrates generating of protein arrays.

FIGURES 9 (A) and (B) present AFM images of anti-chicken IgG AF 488 nanoarrays on Au (A) and silicon (B) surfaces generated by matrix assisted (MA) -DPN.

FIGURE 10 shows fluorescence microscopy images of anti-chicken IgG AF 488 nanoarrays generated by MA-DPN on silicon substrates.

Figure 11. (A) Plots showing the relationship of the DPN-generated dot sizes with tip-substrate contact time of selected ink materials, the slopes of the plot reflect the according ink's diffusion constant. (B) Charts showing the change of the ink (anti-ubiquitin) diffusion rate with the adding of PEO at different ratios. (C) Comparison of the diffusion rate of BSA/PEO and anti-ubiquitin/PEO at ratio of 1:5, the chart shows very close diffusion rate. (D) Charts showing that the ink diffusion rate of IgG and β -galactosidase can be tuned to be very close at the ink/PEG ratio of 1:5 and 1:7.5, respectively.

Figure 12. (A) Fluorescent image of DPN generated dot arrays. The AFM tips were coated one after another with BSA/PEG (green) and anti-ubiquitin/PEG (red), respectively, both at ratio of 1:5, and both inks were simultaneously patterned using passive one dimensional A-26 AFM tip array. (B) Zoomed-in image of the area within the rectangular in (A), which shows sharp fluorescent signal

contrast. (C) and (E), AFM images of DPN generated nanoarrays containing IgG/PEG (1 :5) and β -galactosidase/PEG (1 :7.5), respectively. (D) and (F), fluorescent images of the nanoarrays in (C) and (E) after incubating with according fluorescent labeled antibodies.

Figure 13. (A) Overview and (B) zoomed-in area of the inkwell that used for alternative two ink (BSA/PEG and anti-ubiquitin/PEG) coating. (C) Optical and (D) fluorescent microscopy images of the AFM tip array (A-26) used for multiple-ink patterning by DPN. (E) Overview and (F) zoomed-in area of the inkwell that used for IgG/PEG and β -galactosidase/PEG coating. Inkwell and tip arrays available from Nanolnk, Inc. (Skokie, IL).

DETAILED DESCRIPTION

INTRODUCTION

Nanolithography instruments and accessories, including ink wells and pen arrays, for direct-write printing can be obtained from Nanolnk, Inc., Chicago, IL. DIP PEN NANOLITHOGRAPHY® and DPN® are registered Nanolnk, Inc. trademarks.

The following patents and co-pending applications relate to direct-write printing with use of for example cantilevers, tips, and patterning compounds:

U.S. patent No.6,635,311 issued October 21, 2003 ("Methods Utilizing Scanning Probe Microscope Tips and Products Therefor or Produced Thereby") to Mirkin et al., which describes fundamental aspects of DPN printing including inks, tips, substrates, and other instrumentation parameters and patterning methods;

U.S. patent No. 6,827,979 issued December 7, 2004 ("Methods Utilizing Scanning Probe Microscope Tips and Products Therefor or Produced Thereby") to Mirkin et al., which further

describes fundamental aspects of DPN printing including software control, etching procedures, nanoplotters, and arrays formation.

U.S. patent publication number 2002/0122873 A1 published September 5, 2002 ("Nanolithography Methods and Products Produced Therefor and Produced Thereby"), which describes aperture embodiments and driving force embodiments of DPN printing.

U.S. patent publication 2003/0185967 to Eby et al., published October 2, 2003 ("Methods and Apparatus for Aligning Patterns on a Substrate"), which describes alignment methods for DPN printing.

U.S. patent No. 7,060,977 to Dupeyrat et al., issued June 13, 2006 ("Nanolithographic Calibration Methods"), which describes calibration methods for DPN printing.

U.S. Patent Publication 2003/0068446, published April 10, 2003 to Mirkin et al. ("Protein and Peptide Nanoarrays"), which describes nanoarrays of proteins and peptides;

U.S. Regular Patent Application, Ser. No. 10/307,515 filed Dec. 2, 2002 to Mirkin et al. ("Direct- Write Nanolithographic Deposition of Nucleic Acids from Nanoscopic Tips"), which describes nucleic acid patterning.

U.S. Patent Publication 2003/0162004 to Mirkin et al. published August 28, 2003 ("Patterning of Solid State Features by Direct- Write Nanolithographic Printing"), which describes reactive patterning and sol gel inks.

U.S. Patent No. 6,642,129, issued November 4, 2003, to Liu et al. ("Parallel, Individually Addressible Probes for Nanolithography").

U.S. Patent No. 6,737,646, issued May 18, 2004, to Schwartz ("Enhanced Scanning Probe Microscope and Nanolithographic Methods Using Same").

U.S. Patent No. 6,674,074 issued January 6, 2004, to Schwartz ("Enhanced Scanning Probe Microscope").

U.S. Patent No. 7,098,058 issued August 29, 2006. U.S. Patent publication 2004/0026681 published February 12, 2004. U.S. Patent No. 7,005,378 issued February 28, 2006. U.S. Patent Publication 2004/0175631 published September 9, 2004. U.S. Patent No. 7,034,854 issued April 25, 2006. U.S. Patent Publication 2005/0009206 published January 13, 2005. U.S. Patent Publication 2005/0272885 published December 8, 2005. U.S. Patent Publication 2005/0255237 published November 17, 2005. U.S. Patent Publication 2005/0235869 published October 27, 2005.

U.S. Patent publication 2006/0040057 to Sheehan et al. (Thermal Control of Deposition in Dip Pen Nanolithography). Two dimensional arrays are described in US Patent publication no. 2008/0105042 to Mirkin et al., filed March 23, 2007.

In some embodiments, the direct-write nanolithography methods described herein can be particularly of interest for use in preparing bioarrays, nanoarrays, and microarrays based on peptides, proteins, nucleic acids, DNA, RNA, viruses, and the like. See, for example, US Patent No. 6,787,313 for mass fabrication of chips and libraries; 5,443,791 for automated molecular biology laboratory with pipette tips; 5,981,733 for apparatus for the automated synthesis of molecular arrays in pharmaceutical applications;

Direct write methods, including DPN printing, are described in for example Direct-Write Technologies, Sensors, Electronics, and Integrated Power Sources, Pique and Chrisey (Eds), 2002. Scanning probe microscopy is reviewed in Bottomley, Anal. Chem., 1998, 70, 425R-475R. Scanning probe microscopes are known in the art including probe exchange mechanisms as described in US Patent No. 5,705,814 (Digital Instruments).

The inventors developed a method of patterning utilizing a mixture that comprises a polymer and a nanomaterial. In an embodiment of the method, the mixture is first disposed on a tip or stamp and then transported from the tip or stamp on a substrate surface to form a pattern on the surface that comprises the ink of choice. The method as applied for Dip Pen Nanolithography printing is illustrated on Figure 1.

INK

Ink can be transported to a surface whether from a tip or a stamp or some other transport originating surface. The ink can be a composite material and can comprise at least two components including at least one polymer and at least one nanomaterial, the nanomaterial being different than the polymer. The ink can be initially formulated with use of a solvent and may further comprise solvent or at least residual solvent for the polymer. In many cases, solvent is removed upon disposing the ink at the end of a tip or on a stamp surface. In other cases, the ink yet comprises solvent and is used as a liquid. For example, ink can be delivered by channels to the end of a tip.

A basic and novel feature can be that the ink consists essentially of the polymer and the nanomaterial and is substantially free of components that interfere with transport of polymer and nanomaterial. In some cases, the ink comprises at least at least 70%, or at least 90% by weight

polymer and nanomaterial. The ink can comprises less than 30% by weight or less than 10% by weight material which is not polymer or nanomaterial.

POLYMER

The ink carrier matrix is usually chosen as any material that can be relatively easily patterned by DPN printing. If a specific feature size and particular patterns are desired, the polymer material of the ink carrier matrix can be any material that can be easily patterned by DPN in a well controlled manner as to provide the desired feature size and pattern when used by itself. Preferably, the polymer ink carrier matrix is selected to be such that it satisfies at least some of the following criteria:

- 1) the polymer ink carrier matrix does not chemically react with either the molecules of the ink or the material of the tip or stamp;
- 2) a transport rate of the polymer ink carrier matrix is a higher than a transport rate of the ink mixed with the matrix;
- 3) the polymer ink carrier matrix does not interfere with inherent physical or biological characteristics of the ink.

The ink carrier matrix can be, for example, a polymer matrix. The polymer can be a non-biological polymer. The polymer can be a soluble polymer; it can be a linear polymer having a linear polymer backbone or only small amount of branching. The polymer can be a copolymer, a block copolymer, a random copolymer, a terpolymer, or a branched polymer. A polymer can be functionalized for crosslinking although in many cases this is not desired, particularly if the polymer is to removed by solvent washing.

The polymer can be soluble in both water as well as organic solvent or nonaqueous solvent. A polymer forming the polymer matrix can be, for example, polyalkylene oxide, polyalkylene glycol, or polyalkylene imine. In some embodiments, polyalkylene oxide used as a polymer matrix can be a polyalkylene oxide having a molecular weight over 50,000. Yet, in some embodiments, a polyalkylene oxide having a molecular weight of about 50,000 or less can be used.

In some embodiments, polyethylene oxide (PEO) having a molecular weight (MW) of about 100,000 can be preferred as a material for the polymer matrix. Such a polymer has a low melting temperature and can be easily patterned by itself using DPN. In general, PEO does not react with many hard inks or biomaterials and thus does not effect their chemical, biological or physical characteristics. In addition, PEO is soluble in a variety of solvents including both hydrophilic and hydrophobic solvents, both aqueous and organic solvents, both polar and non-polar solvents. The good solubility makes PEO compatible with a variety of inks. For example, fullerenes or carbon nanotubes can be mixed with PEO using toluene as a common solvent; magnetic nanoparticles can be mixed with PEO using dichloromethane as a common solvents; Au nanoparticles or water soluble conducting polymers, such as sulphonated polyaniline (SPAN) or doped polypyrrole, can be mixed with PEO using water as a common solvent; quantum dots can be mixed with PEO using hexane as a common solvent; biomolecules such as nucleic acids or proteins can be mixed with PEO utilizing an appropriate biological buffer as a common solvent. Moreover, PEO can be patterned on a variety of substrate surfaces including metal surfaces such as Au surface, semiconductor surfaces such as GaAs or InAs surface or oxide surface such as SiO_x surface. Lower molecular weight PEO, also sometimes called polyethylene glycol, can be used.

The polymer and substrate surface can be adapted so that the polymer does not chemisorb to or covalently bond with the surface. Also, the polymer and the nanomaterial can be adapted so that the polymer is not chemically reactive with the nanomaterial.

NANOMATERIAL

Nanomaterials can be particulate types of materials having at least one lateral dimension of at least about 100 nm or less, or about 50 nm or less, or about 25 nm or less. The nanomaterial can be for example a spherical material, or a substantially spherical material, or an elongated material. For example, a fullerene for purposes here can be considered a substantially spherical material. This lateral dimension can be a statistical average for many distinct units or particles. It can be for example an average particle diameter for substantially spherical particles or an average particle length or width for elongated particles. The nanomaterial can be organic or inorganic, hard or soft, flexible or rigid. The nanomaterial can be a non-molecular material. In preferred embodiments, the nanomaterial can be for example a metal nanoparticle, a magnetic nanoparticle, or a fullerene nanoparticle.

While the methods described herein can be applied to delivery of a wide variety of ink nanomaterials, in many cases, the ink nanomaterial can be a material that is difficult to pattern by itself, without a polymer as ink carrier matrix, using DPN printing for example. For example, the transport rate may be too slow or the transporting too unreliable. For instance, the ink of choice can be a hard ink including metal nanoparticles such as Au or Ag silver nanoparticles, semiconductor nanoparticles as quantum dots, oxide nanoparticles such as silica or alumina particles, magnetic particles, carbon-based particles such as fullerenes and carbon nanotubes, crystalline polymers including crystalline conducting polymers. The method is not limited to patterning hard inks and can be used also for patterning soft inks including biomaterials, biomolecules, or biological macromolecules such as nucleic acids, DNA, RNA, proteins, peptides, polypeptides, antibodies, and oligo- and polysaccharides. Crystallized conducting polymer can be used.

In an embodiment, the nanomaterial comprises a nanoparticle nanomaterial. The nanomaterial can comprise a nanoparticle comprising an average particle size of about 2 nm to about 100 nm, or about 2 nm to about 25 nm. In other embodiments, the nanomaterial can be a carbon nanotube, whether single, double, or multi-walled. The nanomaterial can comprise a nanowire or a nanorod. The nanomaterial can comprise a semiconductor-related material and be for example a quantum dot. The nanomaterial and substrate surface can be adapted so that the nanomaterial does not chemisorb to or covalently bond with the surface.

TIPS AND STAMPS

The tip embodiment will be further described. The stamp embodiment will also be further described. Many of the parameters described herein such as the selection of the patterning compound, surface, and contact conditions can be used for both tip and stamp embodiments. Tips and stamps are used in other technologies besides DPN printing and microcontact printing. Tips known in art of DPN printing can be used. Sharp tips can be used which are characterized by a sharp, pointed end. The tip can be for example a nanoscopic tip. The tip can be for example a scanning probe microscope tip or an atomic force microscope tip.

Tips can be engineered to be useful for scanning probe or AFM measurements if suitably adapted with for example cantilever and feedback mechanism. In particular, the tip can be disposed at the end of a cantilever. The tip can be a hollow tip or a solid tip or a non-hollow tip. The tip can comprise a channel for delivery of the ink mixture. Tips including solid, non-hollow, and hollow tips are further described in for example US Patent Nos. 6,635,311 and 6,827,979, as well as 2002/0122873. WO 2005/115630 to Henderson et al, published December 8, 2005, also describes an elongated beam with elongated aperture for deposition on surfaces. See also US Patent Publication 2006/0096078 to Bergaud et al. for deposition based on slit or groove technology; see also, Espinosa

et al., *Small*, 1, No. 6, 632-635, 2005 for nanofountain probe writing; Lewis et al., *Appl. Phys. Lett.*, 1999, 75, 2689-2691; Taha et al., *Appl. Phys. Lett.*, 2003, 83, 1041-1043; Hong et al, *Appl. Phys. Lett.*, 2000, 77, 2604-2606; Meister et al., *Microelectron. Eng.*, 2003, 67-68, 644-650; Deladi et al., *Appl. Phys. Lett.*, 85, 5361-5363.

Tips can comprise hard inorganic, ceramic materials, or softer organic materials. Semiconductor materials can be used. Insulative and conductive materials can be used. Tips known in the art of AFM imaging, for example, can be used including silicon or silicon nitride. For example, polymer or polymer-coated tips can be used. See, for example, US Patent Publication No. 2005/0255237 to Zhang et al. Polymer tips and cantilevers are described in, for example, Mirkin and Liu, US Patent Publication No. 2004/0228962, related to scanning probe contact printing. The tip disposed on the cantilever can be part of a larger structure comprising a plurality of tips disposed on a plurality of cantilevers. These can be called multipen structures or parallel pen structures. For example, the multipen structure can have over 20, or over 100, or over 1,000, or over 10,000, or over 100,000, or over 1,000,000 individual tips. The cantilevers and tips can be adapted for individual actuation, wherein one tip can be raised or lowered independently of another tip. Individual actuation is described in for example US Patent Nos. 6,867,443 and 6,642,129 to Liu et al.,. Electrostatic or thermal actuation can be used. Tips can be thermally heated and activated for temperature control. In particular, the tip can be heated to effect transport. Tips can comprise an inorganic surface and tips can be used where they are not modified after fabrication with an organic material or coating. In one embodiment, a plurality of tips can be provided comprising ink disposed at the end of the tip, and transporting ink from the tips to the substrate surface forms a plurality of structures on the surface comprising both the polymer and the nanomaterial.

In addition, stamps can be used including stamps for microcontact printing can be used. See for example Xia and Whitesides, "Soft Lithography," *Angew. Chem. Int. Ed.*, 1998, 37, 550-575, and

references cited therein, for description of microcontact printing including stamps (pages 558-563). In general, stamps are fabricated for massive parallel printing using Z direction motion rather than serial motions with fine XY motion. Stamps can comprise a single material or can be formed by multilayering methods including surface treatments to improve printing. One surface layer can be supported which has different properties than the support, e.g., stiffer. The stamp can comprise a polymer including an elastomer or a crosslinked rubber, such as, for example, a hydrophobic polymer, such as a silicone polymer or siloxane polymer, which is adapted for accepting ink but also depositing ink. The stamp can be patterned to form lines, including straight and curvilinear lines, or circles or dots. The stamp can be fabricated to have very small structures, which can be a tip. In addition, surfaces can be used which provide relief structures. Here, some areas of the surface rise above other areas of the surface, and the ink primarily coats the raised up areas. One of the advantages of the present method is that it does not require chemical or physical modification of the tip or stamp. I.e. in some embodiments, the tip or stamp can be an unmodified tip or stamp, i.e. a tip or stamp not exposed to chemical or physical modification prior to having a mixture comprising an ink and ink carrying matrix being disposed on the tip or stamp.

The chemical or physical modification of the tip or stamp is usually used in the prior art methods to promote or enhance ink coating to the tip or stamp, to promote or enhance ink adhesion to the tip or stamp and/or to promote or enhance ink transport from the tip or stamp to the substrate surface. Examples of chemical or physical modification of the tip or stamp include but not limited to base treatment to impart a charged surface of the silicon nitride tip, silinization with amino- or mercaptosilanizing agents, non-covalent modification with small molecules or polymeric agents such as polyethyleneglycol (PEG).

SUBSTRATE SURFACE

The substrate surface can be a surface of any substrate although the surface can be adapted to function with the ink, the polymer, the nanomaterial, and the application at hand. Smother substrates are generally preferred for providing pattern's higher resolution. For example, the substrate surface can be a surface of an insulator such as, for example, glass or a conductor such as, for example, metal, including gold. In addition, the substrate can be a metal, a semiconductor, a magnetic material, a polymer material, a polymer-coated substrate, or a superconductor material. The substrate can be previously treated with one or more adsorbates. Still further, examples of suitable substrates include but are not limited to, metals, ceramics, metal oxides, semiconductor materials, magnetic materials, polymers or polymer coated substrates, superconductor materials, polystyrene, and glass. Metals include, but are not limited to gold, silver, aluminum, copper, platinum and palladium. Other substrates onto which compounds may be patterned include, but are not limited to silica, silicon oxide SiO_x , GaAs, InP and InAs. One of the advantages of the present method is that it does not require for a substrate surface to be chemical or physical modified prior to transporting the mixture comprising the ink and the ink carrier matrix to the substrate surface. Accordingly, in some embodiments, the substrate surface can be an unmodified substrate surface, i.e. a substrate surface, which was not chemically or physically modified prior to being patterned.

The chemical or physical medication of the substrate surface is usually used in the prior art methods to promote ink transport from the tip or stamp to the substrate surface, to enhance ink adhesion to the substrate surface or to covalently modify the substrate surface. Examples of physical or chemical modification of the substrate surface include but not limited to base treatment of a charged surface of silicon oxide, silanization with amino or mercaptosilinating agents or modification with polymers carrying chemically reactive groups. Another advantage of the present method that it does not require pre patterning of the substrate surface. The substrate can be monolithic or comprise multiple materials including multiple layers. In a preferred embodiment, the substrate surface is a semiconductor or metal substrate surface. The substrate surface can present conductive portions,

insulative portions, or both. The conductive portions can be electrodes for example. The ink can be transported onto or in between electrodes, establishing contact with electrodes.

INK TRANSPORT

The mixture can be transported from a tip or stamp to a substrate surface in several different ways and is not in particular limited. Known methods in DPN printing and microcontact printing can be used. For instance, in scanning probe and AFM-related technology, different modes can be used to have tips interact with surfaces, which include contact mode, non-contact mode and intermittent contact mode or tapping mode. Cantilevers can be oscillated. Known feedback methods can be used for positioning and alignment the X, Y and Z directions. The transporting of the mixture from the tip to the surface can be carried out by moving the tip only in the Z direction up and down with respect to the XY plane of the substrate surface to engage with and disengage with the surface. A contact time can be used and if contact is what activates ink flow then ink flows during the the contact time. The mixture delivery can be performed without translating the tip over the substrate surface, without moving in the XY plane, and holding the tip stationary. Alternatively, the tip can be translated over the surface, moving in the XY plane. Either the tip can be moved and the surface held stationary, or the surface can be moved and the tip held stationary. The transporting can be carried out under conditions such as humidity, temperature, and gaseous atmosphere which provide for a water meniscus between the tip and surface. For example, relative humidity can be at least about 25%, or at least about 40%, or at least about 50%, or at least about 70%. Conditions can be controlled with use of environmental chambers. The gaseous atmosphere can be air, an inert atmosphere, an atmosphere with controlled humidity, or with the presence of other volatile or gaseous compounds such as vapors of organic compounds or volatile solvents such as alcohols like methanol or ethanol. Conditions can be selected to not favor a water meniscus including, for example, anhydrous conditions or conditions wherein all reagents and surfaces are selected to be free of water.

The transporting can be done manually or by instrument with computer control. Software can be used which can facilitate pattern design, calibration, leveling, and alignment. Calibration methods are described in for example US Patent No. 7,060,977 to Cruchon-Dupeyrat et al. Alignments methods are describe in for example 2003/0185967 to Eby et al. The transporting can be done more than once, repetitively, in either the same spot or at different locations. The ink transport can be characterized by an ink transport rate characterized from transport of mixtures of the polymer and the nanomaterial. The polymer transport can be characterized by a polymer transport rate. The nanomaterial transport can be characterized by a nanomaterial transport rate. The polymer transport rate can be faster than the nanomaterial transport rate. Also, the ink transport rate can be more similar to the polymer transport rate than the nanomaterial transport rate. In the present method, a transport rate of the mixture is dominated by a transport rate of the ink carrier matrix's material, such as PEO. Accordingly, a size such as length, width, and/or height of the formed pattern(s) is determined by the transport rate of the ink carrier matrix's material, which can be controlled either via varying humidity as discussed above or by changing a contact time between the tip and the substrate surface. The ability to write patterns comprising the ink at a rate that can be finely tuned by controlling the transport rater of the ink carrier matrix's material, such as PEO, is one of the advantages of the present method.

OTHER LITHOGRAPHIES BESIDES DPN AND MICROCONT ACT PRINTING

Soft lithographic methods including microcontact printing can be used. See for example Xia and Whitesides, "Soft Lithography," *Angew. Chem. Int. Ed.*, 1998, 37, 550-575. Methods using a patterned elastomeric material as mask, stamp, or mold. Besides microcontact printing, other methods include replica molding (REM), microtransfer molding (μ TM), micromolding in capillaries (MIMIC), and solvent-assisted micromolding (SANIM).

STRUCTURE

The structure formed as a result of the ink transport on the surface can be used as is or treated by additional methods such as heat, light, drying, vacuum, or chemical reaction. Such additional treatment can chemically modify the structure or dry the structure. For example, the polymer can be crosslinked or annealed and morphologically altered. The structure can be washed to remove the polymer, or at least substantially most of the polymer. The structure can be characterized by a lateral dimension such as length, width, diameter such as for example 1 micron or less, or 500 nm or less, or 300 nm or less, or 100 nm or less, or 50 nm or less.

The structure can be a dot or line, and line can be straight or curvilinear. Arbitrary shapes can be formed including rings, squares, and triangles. The structure can have a height which can be for example at least about 5 nm, or at least about 10 nm, or at least about 15 nm, or at least about 20 nm, or at least about 25 nm. The range can be for example about 5 nm to about 100 nm, or about 10 nm to about 50 nm, or about 10 nm to about 25 nm. Height can be used to detect the presence of nanomaterial. For example, the structure can have a height which is at least two times, twice, or at least three times, or at least four times, the height compared to a structure substantially identical prepared except without the nanomaterial.

The structure can comprise polymer and the nanomaterial, as well as residual solvent or moisture. The polymer and the nanomaterial can be substantially evenly distributed, or they can phase separate. The methods can be repeated to provide a plurality of structures on the surface including for example array formation comprising at least two, at least 50, at least 100, at least 500, at least 1,000, or at least 50,000 structures on a single surface.

ARRAYS

The method can be particularly useful for the preparation of nanoarrays, arrays on the submicrometer scale having nanoscopic features when used with DIP PEN™ nanolithographic printing. Preferably, a plurality of dots or a plurality of lines are formed on a substrate. The plurality of dots can be a lattice of dots including hexagonal or square lattices as known in the art. The plurality of lines can form a grid, including perpendicular and parallel arrangements of the lines.

The lateral dimensions of the individual patterns including dot diameters and the line widths can be, for example, about 2,000 or less, about 1,000 nm or less, about 500 nm or less, about 300 nm or less, and more particularly about 100 nm or less. The range in dimension can be, for example, about 1 nm to about 750 nm, about 10 nm to about 2,000 nm, about 10 nm to about 500 nm, and more particularly about 100 nm to about 350 nm. The number of patterns in the plurality of patterns is not particularly limited. It can be, for example, at least 10, at least 100, at least 1,000, at least 10,000, even at least 100,000. Square arrangements are possible such as, for example, a 10 X 10 array. High density arrays can be preferred.

The distance between the individual patterns on the nanoarray can vary and is not particularly limited. For example, the patterns can be separated by distances of less than one micron or more than one micron. The distance can be, for example, about 300 to about 1,500 microns, or about 500 microns to about 1,000 microns. Distance between separated patterns can be measured from the center of the pattern such as the center of a dot or the middle of a line.

The methods described herein can be repeated to provide a plurality of structures on the surface which are separated from each other by less than a micron. The method can be also applied for forming patterns of larger scales such as micron scale, millimeter scale or centimeter scale. Such larger patterns can be prepared, for example, utilizing microcontact printing for transporting the

mixture comprising the ink of choice and the ink carrier matrix from a microcontact printing stamp to the substrate surface.

ARRAYS OF NANO-BUILDING BLOCKS

The method can be applied for patterning hard inks including but not limited to metal nanoparticles, such as Au or Ag silver nanoparticles; semiconductor nanoparticles, such as quantum dots; oxide nanoparticles, such as silica or alumina particles; magnetic particles; carbon-based particles, such as fullerenes and carbon nanotubes, crystalline polymers including crystalline conducting polymers. The method can be particularly useful for forming hard ink arrays. Such hard ink arrays comprise a substrate and a plurality of patterns that comprise a hard ink of choice and a ink carrier matrix. When the hard ink of choice comprises carbon based material such as fullerene, the hard ink array can serve as an electronic device such as a transistor.

BIOARRAYS

The method can applied for patterning biomaterials such as nucleic acids, proteins or oligo or polysaccharides. In this case, the mixture comprises an ink that is a biomaterial of choice and an ink carrier matrix which can be a polymer such as polyalkylene oxide or poly alkylene imine. In some embodiments, the biomolecule can comprise various kinds of chemical structures comprising peptide bonds. These include peptides, proteins, oligopeptides, and polypeptides, be they simple or complex. The peptide unit can be in combination with non-peptide units. The protein or peptide can contain a single polypeptide chain or multiple polypeptide chains. Higher molecular weight peptides are preferred in general although lower molecular weight peptides including oligopeptides can be used. The number of peptide bonds in the peptide can be, for example, at least three, ten or less, at least 100, about 100 to about 300, or at least 500. Proteins are particularly preferred. The protein can be simple

or conjugated. Examples of conjugated proteins include, but are not limited to, nucleoproteins, lipoproteins, phosphoproteins, metalloproteins and glycoproteins.

Proteins can be functional when they coexist in a complex with other proteins, polypeptides or peptides. The protein can be a virus, which can be complexes of proteins and nucleic acids, be they of the DNA or RNA types. The protein can be a shell to larger structures such as spheres and rod structures. Proteins can be globular or fibrous in conformation. The latter are generally tough materials that are typically insoluble in water. They can comprise a polypeptide chain or chains arranged in parallel as in, for example, a fiber. Examples include collagen and elastin. Globular proteins are polypeptides that are tightly folded into spherical or globular shapes and are mostly soluble in aqueous systems. Many enzymes, for instance, are globular proteins, as are antibodies, some hormones and transport proteins, like serum albumin and hemoglobin. Proteins can be used which have both fibrous and globular properties, like myosin and fibrinogen, which are tough, rod-like structures but are soluble. The proteins can possess more than one polypeptide chain, and can be oligomeric proteins, their individual components being called protomers. The oligomeric proteins usually contain an even number of polypeptide chains, not normally covalently linked to one another. Hemoglobin is an example of an oligomeric protein. Types of proteins that can be incorporated into a nanoarray of the present invention include, but are not limited to, enzymes, storage proteins, transport proteins, contractile proteins, protective proteins, toxins, hormones and structural proteins. Examples of enzymes include, but are not limited to ribonucleases, cytochrome c, lysozymes, proteases, kinases, polymerases, exonucleases and endonucleases. Enzymes and their binding mechanisms are disclosed, for example, in *Enzyme Structure and Mechanism*, 2nd Ed., by Alan Fersht, 1977 including in Chapter 15 the following enzyme types: dehydrogenases, proteases, ribonuc leases, staphylococcal nucleases, lysozymes, carbonic anhydrases, and triosephosphate isomerase. Examples of storage proteins include, but are not limited to ovalbumin, casein, ferritin, gliadin, and zein. Examples of transport proteins include, but are not limited to hemoglobin, hemocyanin, myoglobin, serum albumin, β l -

lipoprotein, iron-binding globulin, ceruloplasmin. Examples of contractile proteins include, but are not limited to myosin, actin, dynein. Examples of protective proteins include, but are not limited to antibodies, complement proteins, fibrinogen and thrombin.

Examples of toxins include, but are not limited to, Clostridium botulinum toxin, diphtheria toxin, snake venoms and ricin. Examples of hormones include, but are not limited to, insulin, adrenocorticotrophic hormone and insulin-like growth hormone, and growth hormone. Examples of structural proteins include, but are not limited to, viral-coat proteins, glycoproteins, membrane-structure proteins, α -keratin, sclerotin, fibroin, collagen, elastin and mucoproteins. Natural or synthetic peptides and proteins can be used. Proteins can be used, for example, which are prepared by recombinant methods. Examples of preferred proteins include immunoglobulins, IgG (rabbit, human, mouse, and the like), Protein A/G, fibrinogen, fibronectin, lysozymes, streptavidin, avidin, ferritin, lectin (Con. A), and BSA. Rabbit IgG and rabbit anti-IgG, bound in sandwich configuration to IgG are useful examples. Spliceosomes and ribozymes and the like can be used. A wide variety of proteins are known to those of skill in the art and can be used. See, for instance, Chapter 3, "Proteins and their Biological Functions: A Survey," at pages 55-66 of BIOCHEMISTRY by A. L. Lehninger, 1970.

One of the advantages of the method is that it does not require pre patterning of the substrate surface with a patterning compound prior to transporting a mixture comprising the protein from the tip to the surface when forming submicron size patterns, i.e. patterns with features having a lateral dimension of less than about 1 micron, or sub 100 nm patterns, i.e. patterns having a lateral dimension of less than about 100 nm. Patterning compounds were used by the prior art methods to improve stability of protein containing submicron or sub 100 nm features. Examples of patterning compounds include a sulfur-containing compound such as, for example, a thiol, polythiol, sulfide, cyclic disulfide, a sulfur-containing compound having a sulfur group at one

end and a terminal reactive group at the other end, such as an alkane thiol with a carboxylic acid end group. Additional patterning compounds are disclosed in US patent publication 2003/0068446 published April 10, 2003, to Mirkin et. al. Non-specific binding of proteins to the regions of the substrate surface, can be prevented by covering, or "passivating," those regions of the substrate surface that were not exposed to the mixture comprising the biomolecule and the ink carrier matrix with one or more passivating compounds. Known passivating compounds can be used and the invention is not particularly limited by this feature to the extent that non-specific adsorption does not occur.

A variety of passivating compounds can be used including, for example, surfactants such as alkylene glycols which are functionalized to adsorb to the substrate. An example of a compound useful for passivating is 11-mercaptoundecyl-tri(ethylene glycol). Proteins can have a relatively weak affinity for surfaces coated with 11-mercaptoundecyl-tri(ethylene glycol) and therefore do not bind to such surfaces. See, for instance, Browning-Kelley et al, *Langmuir* 13, 343, 1997; Waud-Mesthrige et al, *Langmuir* 15, 8580, 1999; Waud- Mesthrige et al, *Biophys. J.* 80 1891, 2001; Kenseth et al, *Langmuir* 17, 4105, 2001; Prime & Whitesides, *Science* 252, 1164, 1991; and Lopez et al, *J.Am.Chem.Soc.* 115, 10774, 1993. However, other chemicals and compounds, such as bovine serum albumin (BSA) and powdered milk, that can be used to cover a surface in similar fashion to prevent non-specific binding of proteins to the substrate surface. BSA, however, can provide less performance than 11-mercaptoundecyl-tri(ethylene glycol). After passivation, the resultant array can be called a passivated array of proteins or peptides. After passivation, the matrix can be washed away from the patterned regions on the surface. The use of polyalkylene oxide as the matrix allows retaining the biological activity of the biomaterial in the patterned regions upon washing away the matrix. One embodiment of making protein array according to the method is illustrated in Figure 8.

APPLICATIONS

Biological, diagnostic, assays, sensors, semiconductor, electronic, photomask repair, transistor fabrication and repair, including field effect transistors, flat panel display fabrication and repair, and magnetic applications can be benefited with use of the various embodiments described herein. Many applications of DPN printing are described in Ginger, Zhang, and Mirkin, "The Evolution of Dip Pen Nanolithography," *Angew. Chem. Int. Ed.*, 2004, 43, 30-45. Applications for microcontact printing are described in for example Xia and Whitesides, "Soft Lithography," *Angew. Chem. Int. Ed.*, 1998, 37, 550-575, and references cited therein. Biological applications include assays, diagnostics, sensor, protein microarrays, nucleic acid and DNA microarrays, nanoarrays, cell adhesion and growth, and the like. Biodiagnostic applications are described in for example Rose & Mirkin, "Nanostructures in Biodiagnostics," *Chem. Rev.*, 2005, 105, 1547-1562, which is hereby in its entirety. DNA microarrays are described in *DNA Microarrays, A Practical Approach*, Ed. Schena, 1999, Oxford University Press. Applications for protein and peptide nanoarrays are described in for example US Patent Publication No. 2003/0068446 to Mirkin et al. For example, surfaces can be patterned with compounds adapted for capturing a variety of proteins and peptide structures. Further assays can be developed including for example testing for diseases such as HIV. See for example Lee et al, "Nano-Immunoassays for Ultrahigh Sensitive/Selective Detection of HIV," *NanoLett.* 2004, 4, 1869-1872. This describes patterning of MHA, which is then deprotonated so features are negatively charged. Monoclonal antibodies to the HIV-I p24 antigen are then immobilized on the MHA and then exposed to plasma samples taken from infected patients.

Nanoparticle probes can be used to detect and amplify the signal. In these and other biological applications, surfaces can be passivated to prevent non-specific binding including non-specific protein binding. See also US Patent Publication No. 2005/0009206 to Mirkin et al. In field effect transistor applications, sources, drains, gates, electrodes, and channels can be fabricated by methods known in the arts.

The invention is further illustrated by, though in no way limited to, the following working examples.

WORKING EXAMPLES 1. Materials and Instrumentation

Polyethylene oxide (PEO, MW = 100,000), polyethylene glycol (PEG, MW = 8,000), and polyethyleneimine (PEI, MW = 2,000) were purchased from Sigma- Aldrich (Milwaukee, WI). Au nanoparticles (AuNP) solutions were obtained from Ted Pella (Redding, CA). Magnetic nanoparticles (MNP) were synthesized. Fullerene was purchased from Mer Corporation (Tucson, AZ). Acetonitrile, dichloromethane, toluene were purchased from Fisher Scientific (Fairlawn, NJ). All chemicals were used as received. Si/SiO_x wafer with 500 nm oxide coating layer were purchased from WaferNet, Inc. (San Jose, CA). Gold substrates were obtained by thermal evaporation of a gold thin film (30 nm) on a Si/SiO_x substrate pre-coated with a Ti adhesion layer (7 nm). GaAs and InAs wafers were purchased from Wafer World Inc. (West Palm Beach, FL). All DPN experiments were performed on a ThermoMicroscopes CP AFM (Veeco Instruments Inc., CA), which was enclosed in a humidity-controlled chamber and driven by commercially available DPN software (Nanolnk Inc., Chicago, IL). The humidity was controlled at 70% for all PEO related experiments, and 50% for PEI experiments. AFM probes (S-1 or S-2) were purchased from Nanolnk Inc., with spring constants of 0.041 N/m and 0.1 N/m, respectively. MFM data were obtained with a DI multimode SPM (Veeco Instruments Inc., CA), using a pre-magnetized AFM probe.

Preparation of Inks

For all DPN experiments, PEO and PEG solutions (16 mg/mL) were made by dissolving PEO in acetonitrile, dichloromethane, water, or toluene. To prepare the AuNP/PEO ink, PEO (16 mg/mL) in acetonitrile was mixed with a AuNP solution at a volume ratio of 1 : 1 (2 ran AuNP), 2:1 (5 nm AuNP), and 4:1 (13 nm AuNP). To prepare the 4.7 nm MNP/PEO solution, PEO (16 mg/mL) in dichloromethane was mixed with a MNP solution at a volume ratio of 2: 1. To prepare the

fullerene/PEO ink, PEO (16 mg/ml) in toluene was mixed with a saturated fullerene solution in toluene at a volume ratio of 1 :2. To prepare the 2 nm AuNP/PEI ink, a 5% diluted PEI water solution was mixed with a 2 nm AuNP solution at the volume ratio of 1:1.2. Matrix- Assisted DPN of nanobuilding blocks

A. Polymer only controls. FIG. 2 shows control patterns of polyethylene glycol (PEG, MW 8,000), polyethylene oxide (PEO, MW 100,000), and polyethylene imine (PEI, MW 2000) created using DPN on several types of substrates. In particular, FIG. 2 A and FIG. 2B present topographic AFM images of DPN-generated PEG patterns on Au (writing speed of $0.16 \mu\text{m/s}$) and GaAs (writing speed of $0.022 \mu\text{m/s}$), respectively. FIG. 2C and FIG. 2D show DPN-generated PEO patterns on SiO_x and Au respectively with writing speed of $0.05 \mu\text{m/s}$ for both. FIG. 2E demonstrates direct patterning of PEI with writing speeds of 0.6 and $0.3 \mu\text{m/s}$ on an InAs substrate. The corresponding height profile in FIG. 3A shows that different writing speeds result in different pattern heights. The faster writing speed ($0.6 \mu\text{m/s}$) produces smaller height (1.75 nm), while the slower writing speed ($0.3 \mu\text{m/s}$) produces bigger height (2.75 nm). FIG 2F demonstrates the ability of PEI to act as a carrier matrix by presenting DPN patterns of a mixture of PEI and 2 nm Au nanoparticles on an InAs substrate produced with writing speeds of 0.1 and $0.05 \mu\text{m/s}$. The corresponding height profiles in FIG 3B demonstrate that $0.1 \mu\text{m/s}$ writing speed produces pattern having height of 12 nm, while $0.05 \mu\text{m/s}$ writing speed produces pattern having height of 14 nm. Comparison of the height profiles demonstrates that the pattern of the mixture containing 2 nm Au nanoparticles is distinctly greater than that of PEI only. This indicates the presence of Au nanoparticles in the patterns prepared from the mixture containing Au nanoparticles.

B. Au nanoparticles. The capability of these polymers to act as carrier matrices was demonstrated for common nanomaterials. Specifically, FIG. 4 shows arrays of Au nanoparticles (AuNP) generated using direct single-step patterning process. As a control, FIG. 4A shows a

topographic AFM image of dot arrays produced using PEO only, with tip- substrate contact times of 64, 32, and 16 seconds from top to bottom respectively. The feature heights of the obtained dot arrays are 8.5, 3.3, and 1.7 nm for contact times of 64, 32, and 16 seconds respectively, see TABLE 1. FIG. 4A, FIG. 4B nad and FIG. 4C are topographic AFM images of DPN generated dot arrays of 2, 5, and 13 nm Au nanoparticless mixed with PEO respectively. TABLE 1 lists the heights of these structures. Clearly, all of the nanoscale features containing Au nanoparticles are much greater in height than those of only PEO. The height increase is larger for patterns containing nanoparticles of bigger diameters. In a similar manner, a mixture of 5 nm Au nanoparticles and PEO was patterned on a Transmission Electron Microscope (TEM) grid. The inset of Fig. 3E, which is a TEM image of a DPN generated dot on the TEM grid, demonstrates clusters of Au nanoparticles, which proves the presence of Au nanoparticles in these patterns.

Table 1

Contact	Heights of DPN generated dot features, nm					
time, s	PEO only	MNP/PEO	AuNP/PEO 2 nm	AuNP/PEO 5 nm	AuNP/PEO 13 nm	C ₆₀ /PEO
64	8.5	27.4	20.8	25.8	32.3	21.8
32	3.3	23.1	13.8	16.1	23.5	14.6
16	1.7	18.3	8.6	10.6	18.5	9.8

C. Magnetic nanoparticles. Patterns of magnetic nanoparticles (MNP) were also created using a matrix-assisted DPN. FIG. 5 features the patterns containing 4.7 nm magnetic nanoparticles (MNP) prepared using PEO as a carrier matrix. FIG. 5A and FIG. 5B are topography AFM images of DPN-generated dot arrays with tip substrate contact of 64, 32, and 16 sec from top to bottom, and diamond-shape line patterns at writing speed of 0.05 $\mu\text{m/s}$, respectively. Again, an obvious height difference was observed when comparing the heights of these patterns with those of pure PEO, see TABLE 1. The increased height for patterns prepared from mixtures containing MNPs indicates the MNPs are

embedded in these patterns. To further prove the presence of the MNPs inside patterns prepared from a mixture containing MNPs, the patterns were further characterized using Magnetic Force Microscopy (MFM), a technique which shows clear contrast based on the magnetism of the sample. In the MFM images in FIG. 5C and FIG. 5D, the patterned features containing MNPs can be undoubtedly distinguished from the non-magnetic bare SiO_x substrate. This strong contrast even is observed for a single feature, see insets in FIG. 5C and FIG. 5D indicating that magnetic particles were evenly distributed throughout the entire patterned feature. The MFM image of a single line pattern, see inset in FIG. 5D shows magnetic clusters inside the pattern. These kinds of clusters are not observed in patterns of pure PEO. This observation indicates that these clusters are pockets of MNPs. The large area patterns presented in FIG. 4 (C)- (D) also demonstrate that the matrix assisted DPN can provide extended writing times as well as smooth and well-controlled ink transfer rate.

D. Fullerenes. In addition to Au nanoparticles and magnetic nanoparticles, DPN patterns of carbon-based nanomaterials (fullerenes) were also generated using PEO as a carrier. The ability to pattern fullerenes is particularly important due to their potential application in nanoelectronics (71). FIG. 6 shows DPN-generated nanoarrays of a mixture of fullerene and PEO. FIG. 6A shows a dot array with tip-substrate contact times of 16, 8, and 4 s (top to bottom). 80 nanometer feature sizes were easily created at the 4 second contact time (FIG. 6A), proving that sub- 100 nm features can be obtained easily using this technique. With contact times of 64, 32, and 16 s, features of 21.8, 14.6 and 9.8 nm in height were produced, see TABLE 1 and a topography AFM image and corresponding height profile in FIG. 7A and FIG. 7B. Again, these heights are greatly increased compared to those of the corresponding pure PEO patterns, indicative of the presence of fullerenes in the DPN dot arrays generated from the mixture containing fullerenes. These same trends regarding height increases, see FIG. 7C, were observed for continuous lines produced using the mixture of fullerene and PEO (writing speeds = 0.05, 0.1, and 0.2 $\mu\text{m/s}$), see FIG. 6B. As a proof-of-concept, as well as to further confirm that fullerene molecules indeed are patterned in these DPN-generated features, the first

fullerene-based transistor was built via DPN. Lines of the fullerene/PEO ink were generated across an EBL-generated nanoelectrode with a gap size of 500 nm. The 3D topographic AFM image in FIG. 6C clearly shows two crossed, continuous lines wired across these gaps. Current- voltage (I- V) measurements monitoring the output current of this device at voltages ranging from - 0.7 V to 0.85 V are shown in FIG. 6D. The black line is a plot of the I-V response of the transistor measured in a dark environment, while the red (gray) line shows the current obtained under illumination with a Xe lamp (150 W). The observed increase in current (~ 6 times more, ~ 0.015 pA at 0.85 V vs. ~ 0.10 pA at 0.85 V) is a characteristic response of fullerene molecules to light illumination (70, 72). Such a response indicates that the photoactive fullerene molecules are present in an active state inside the DPN-generated patterns. In addition, the precise delivery of fullerene/PEO lines within the 500 nm gapped nanoelectrode also demonstrates a high spatial resolution of DPN.

3. Protein nanoarrays.

Nanoarrays of goat anti-chicken IgG Alexafluor 488 were prepared by a matrix assisted DPN as illustrated in the general scheme presented in FIG. 8. A low molecular weight polymer (poly-ethylene glycol, MW = 8000) was used as a matrix to transport anti-chicken IgG AF 488 from the AFM tip to the substrate surface. PEG is an excellent material to resist non-specific protein adsorption on surfaces. The use of PEG as a matrix allows one to wash away PEG after generating protein nanoarray to retain the biological activity of the protein. DPN was performed at a relative humidity of 75% and at 25°C. Unmodified Nanolnk type A tips were dip coated with a mixture containing the antibody and PEG and dried with nitrogen. FIG. 9 A and FIG. 9B demonstrate AFM images of generated nanoarrays of anti-chicken IgG Alexafluor 488 by MA-DPN method on gold and silicon substrates, respectively. The anti-chicken IgG Alexafluor 488 nanoarrays were further characterized by fluorescence microscopy as shown Figure 10. The AFM and fluorescence images clearly indicate that one can generate uniform nanoarrays of proteins using MA-DPN. The matrix encapsulated proteins are shown to be biologically active as indicated by our results with microarrays generated by microcontact printing.

ADDITIONAL EXAMPLES

A significant application of this universal ink is the capability of simultaneous patterning of multiple biomolecules, and the retaining of their bioactivities. As stated previously, each ink has its own diffusion rate, which makes it extremely difficult (if possible) for simultaneous patterning of multiple inks, and further for feature size control via the tip-substrate contact time. Fig. 1 IA shows the ink diffusion rate of PEG as well as four biomolecules in PBS buffer. One can easily see that the ink diffusion rate varies dramatically according to different ink materials selected, which will sequentially become a major issue if we anticipate very similar or identical feature size during simultaneous multiple ink patterning. For example, the slope of pure IgG can be as high as 30.81, while that of anti-ubiquitin is only 11.30, which means at the same tip-substrate contact time (4 sec), the generated dot size will be 439.0 nm for β -galactosidase and 144.7 nm for BSA, which indeed varies a lot. What is more, the different slopes also means that the increase trend of the dot size is also different. However, using the universal ink where PEG works as an ink carrier, the ink diffusion rate can be easily tuned within a certain range. In order to prove this point, we have monitored the ink diffusion rate change of the mixture of anti-ubiquitin/PEG at different ratios (Fig. 1 IB). At anti-ubiquitin:PEG ratio of 1 :2, the diffusion rate of the mixed ink jumps to 28.72 from 11.30, and it further increases to 29.41 at the ratio of 1 :5. Plots in Figs. HC and HD not only give more examples of such capability PEG has, but also show that the diffusion rate of each individual ink can be tuned within certain range, and what is more, we can make two different inks have very similar diffusion rate. This is an important parameter that facilitates the precise control of each ink's final feature size and the sequential size increase trend after multiple-ink DPN patterning since the tip-substrate contact time will always be the same (as the AFM probe array we used is a passive mode). Except the ink carrier capability, another important role PEG plays in the universal ink kit is its ability to tune the ink's diffusion rate. One then used one dimensional AFM tip array (Model No.: A-26, Nanolnk Inc., Skokie, IL) for simultaneous multiple ink patterning via DPN. Two composite inks containing fluorescent labeled BSA (green color) and anti-ubiquitin (red color), were coated in every other AFM

probes, respectively, using the inkwell (Nanolnk Inc., Skokie, IL) that specially designed for such purposes. Both the optical microscopy images of the inkwell we used and the AFM tip arrays before and after ink-coating are shown in Figure 13. The diffusion rates of the two inks were intentionally tuned very similar following the ratio of 1:5 for both BSA:PEG and anti-ubiquitin:PEG shown in Fig. 11C. DPN was done under the same experimental conditions as described in Fig. 11C. The fluorescent images in Fig. 12A clearly proved that two different kinds of biomolecules (BSA in green and anti-ubiquitin in red) were simultaneously patterned into designed array. The zoomed-in image in Fig. 12B shows more details and clear contrast of the fluorescent signal. In order to compare the variation of generated pattern sizes, one took AFM images after DPN experiment to characterize the generated dot sizes. As a representative, at tip-substrate contact time of 32 sec, the average dot diameter is 328.3 nm for BSA and 306.1 nm for anti-ubiquitin, which has only less than 7% variation (AFM images not shown). On the other side, the generated dot sizes would be 284.3 nm and 223.1 nm if not mixed with PEG based on the plots shown in Fig. 11A. To further prove the bioactivities of the patterned biomolecules, we first generated IgG and β -galactosidase patterns individually. Figs. 12C and 12E are AFM images of generated IgG and β -galactosidase dot arrays at tip-substrate contact time of 32 sec. The average dot diameter is 347.2 nm for IgG and 380.3 nm for β -galactosidase, which has around 8% variation. Similarly, the generated biomolecular dot sizes would be 251.0 nm and 439.1 nm, respectively, if without PEG according to Fig. 11A. One then incubated the biomolecular arrays into according antibody buffer solution. The according fluorescent images in Figs. 12D and 12F indicate that both anti-IgG (green) and anti- β -galactosidase (red) can successfully bind on the pre-generated dot arrays of antigen molecules, which means the patterned IgG and β -galactosidase still remain their bioactivities.

LIST OF REFERENCES

1. C. Burda, X. B. Chen, R. Narayanan, M. A. El-Sayed, Chem. Rev. 105, 1025 (2005).
2. X. Wang, J. Zhuang; Q. Peng, Y. D. Li, Nature 437, 121 (2005).
3. W. Kratschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, Nature 347, 354 (1990).
4. M. C. Daniel, D. Astruc, Chem. Rev. 104, 293 (2004).
5. R. Shenhar, V. M. Rotello, Acc. Chem. Res. 36, 549 (2003).
6. S. H. Sun, C. B. Murray, D. Weller, L. Folks, A. Moser, Science 287, 1989 (2000).
7. S. H. Sun, Adv. Mater. 18, 393 (2006).
8. A. P. Alivisatos, Science 271, 933 (1996).
9. L. E. Brus, Appl. Phys. A 53, 465 (1991).
10. R. C. Jin *et al.*, Nature 425, 487 (2003).
11. R. C. Jin *et al.*, Science 294, 1901 (2001).
12. Y. G. Sun, Y. N. Xia, Science 298, 2176 (2002).
13. J. E. Millstone *et al.*, J. Am. Chem. Soc. 127, 5312 (2005).
14. S. S. Shankar *et al.*, Nat. Mater. 3, 482 (2004).
15. T. K. Sau, C. J. Murphy, J. Am. Chem. Soc. 126, 8648 (2004).
16. S. Hachisu, S. Yoshimura, Nature 283, 188 (1980).
17. F. X. Redl, K. S. Cho, C. B. Murray, S. O'Brien, Nature 423, 968 (2003).
18. K. I. Suzuki, Kenichi; Imai, Hiroaki, J. Am. Chem. Soc. 126, 462 (2004).
19. J. A. Nelson, L. H. Bennett, M. J. Wagner, J. Am. Chem. Soc. 124, 2979 (2002).
20. C. W. Scheeren, G. Machado, J. Dupont, P. F. P. Fichtner, S. R. Texeira, Inorg. Chem. 42, 4738 (2003).
21. V. Juttukonda *et al.*, J. Am. Chem. Soc. 128, 420 (2006).
22. D. H. Geho, C. D. Jones, E. F. Petricoin, L. A. Liotta, Curr. Opin. Chem. Biol. 10, 56 (2006).
23. C. C. Lee, D. H. Chen, Nanotechnology 17, 3094 (2006).
24. J. Park *et al.*, Nat. Mater. 3, 891 (2004).

25. X. Z. Lin, X. W. Tang, H. Yang, *Langmuir* 19, 10081 (2003).
26. J. Park *et al.*, *Ang. Chem. Int. Ed.* 44, 2872 (2005).
27. I. Hussain *et al.*, *J. Am. Chem. Soc.* 127, 16398 (2005).
28. M. Chen, J. P. Liu, S. H. Sun, *J. Am. Chem. Soc.* 126, 8394 (2004).
29. Z. L. Wang, J. H. Song, *Science* 312, 242 (2006).
30. Y. Cui, Q. Q. Wei, H. K. Park, C. M. Lieber, *Science* 293, 1289 (2001).
31. Y. Huang *et al.*, *Science* 294, 1313 (2001).
32. C. R. Martin, *Science* 266, 1961 (1994).
33. S. Park, J. H. Lim, S. W. Chung, C. A. Mirkin, *Science* 303, 348 (2004).
34. S. Park, S. W. Chung, C. A. Mirkin, *J. Am. Chem. Soc.* 126, 11772 (2004).
35. C. Z. M. A. Reed, C. J. Muller, T. P. Burgin, J. M. Tour, *Science* 278, 252 (1997).
36. L. D. Qin, S. Park, L. Hunag, C. A. Mirkin, *Science* 309, 113 (2005).
37. C. T. Campbell, *Science* 306, 234 (2004).
38. G. A. Somorjai, A. M. Contreras, M. Montano, R. M. Rioux, *Proc. Natl. Acad. Sci. USA* 103, 10577 (2006).
39. G. M. Whitesides and B. Grzybowski, *Science* 295, 2418 (2002).
40. D. Philp, J. F. Stoddart, *Angew. Chem. Int. Ed.* 35, 1155 (1996).
41. B. A. Grzybowski, H. A. Stone, G. M. Whitesides, *Nature* 405, 1033 (2000).
42. A. Terfort, N. Bowden, G. M. Whitesides, *Nature* 386, 162 (1997).
43. C. A. Mirkin, W. B. Caldwell, *Tetrahedron* 52, 5113 (1996).
44. C. Xue, Z. Li, C. A. Mirkin, *Small* 1, 513 (2005).
45. S. Panigrahi *et al.*, *J. Phys. Chem. B* 110, 13436 (2006).
46. B. A. Grzybowski, A. Winkleman, J. A. Wiles, Y. Brumer, G. M. Whitesides, *Nat. Mater.* 2, 241 (2003).
47. A. M. Kalsin *et al.*, *Science* 312, 420 (2006).
48. T. Cui, F. Hua, Y. Lvov, *Sens. Actuators, A* 114 501 (2004).
49. D. Qin *et al.*, *Adv. Mater.* 11, 1433 (1999).
50. M. K. Corbierre, J. Beerens, R. B. Lennox, *Chem. Mater.* 17, 5774 (2005).
51. K. D. Kloepper, T. D. Onuta, D. Amarie, B. Dragnea, *J. Phys. Chem. B* 108, 2547 (2004).

52. R. Sheparovych *et al.*, Chem. Mater. 18, 591 (2006).
53. W. A. Lopes, H. M. Jaeger, Nature 414, 735 (2001).
54. M. Aizawa, J. M. Buriak, J. Am. Chem. Soc. 128, 5877 (2006).
55. M. Aizawa, J. M. Buriak, J. Am. Chem. Soc. 127, 8932 (2005).
56. L. M. Demers, C. A. Mirkin, Ang. Chem. Int. Ed. 40, 3071 (2001).
57. R. A. McMillan *et al.*, Nat. Mater. 1, 247 (2002).
58. M. G. Warner, J. E. Hutchison, Nat. Mater. 2, 272 (2003).
59. J. C. Garno, N. A. Amro, S. Cruchon-Dupeyrat, S. Chen, G.-Y. Liu, Nano Lett. 3, 389 (2003).
60. D. S. Ginger, H. Zhang, C. A. Mirkin, Ang. Chem. Int. Ed. 43, 30 (2004).
61. K. Salaita *et al.*, Small 1, 940 (2005).
62. K. Salaita, Y. Wang, R. Vega, C. A. Mirkin, submitted to Science.
63. L. Ding, Y. Li, H. B. Chu, X. M. Li, J. Liu, J. Phys. Chem. B 109, 22337 (2005).
64. D. Prime, S. Paul, C. Pearson, M. Green, M. C. Petty, Mater. Sci. & Eng., C 25, 33 (2005).
65. N. S. John, G. Gundiah, P. J. Thomas, G. U. Kulkarni, Int. J. Nanosci. 4, 921 (2005).
66. M. E. Pumarol, Y. Miyahara, R. Gagnon, P. Grutter, Nanotechnology 16, 1083 (2005).
67. Ali, M. B., T. Ondarcuhu, M. Brust, C. Joachim, Langmuir 18, 872 (2002).
68. T. Vijaykumar, N. S. John, G. U. Kulkarni, Solid State Sci. 7, 1475 (2005).
69. L. Huang, J. J. Kakkaserry, C. A. Mirkin, unpublished results.
70. T. L. Makarova, Semiconductors 35, 243 (2001).
71. Park, H. et al. Nanomechanical oscillations in a single-C₆₀ transistor. *Nature* 407, 57-60 (2000).
72. Hamed, A., Sun, Y. Y., Tao, Y. K., Meng, R. L. & Hor, P. H. Effects of Oxygen and Illumination on the in situ Conductivity of C₆₀ Thin Films. *Phys. Rev. B* 47, 10873-10880 (1993).
73. Iijima, S. Helical microtubules of graphitic carbon. *Nature* 354, 56-58 (1991).

74. Orendorff, C. J., Sau, T. K. & Murphy, C. J. Shape-dependent plasmon-resonant gold nanoparticles. *Small* 2, 636-639 (2006).
75. Goldberger, J., Hochbaum, A. I., Fan, R. & Yang, P. Silicon Vertically Integrated Nanowire Field Effect Transistors. *Nano Lett.* 6, 973-977 (2006).
76. Vega, R. A., Maspoch, D., Salaita, K. & Mirkin, C. A. Nanoarrays of Single Virus Particles. *Angew. Chem. Int. Ed.* 44, 6013-6015 (2005).
77. Patolsky, F., Zheng, G. & Lieber, C. M. Nanowire-based biosensors. *Anal. Chem.* 78, 4260-4269 (2006).
78. Kong, J. et al. Nanotube molecular wires as chemical sensors. *Science* 287, 622-625 (2000).
79. Gates, B. D. et al. New Approaches to Nanofabrication. *Chem. Rev.* 105, 1171-1196 (2005).

WHAT IS CLAIMED IS:

1. A method comprising:
 - providing a nanoscopic tip,
 - providing an ink disposed at the end of the nanoscopic tip, wherein the ink comprises at least one nanomaterial and at least one polymer as an ink carrier of the nanomaterial, wherein the at least one polymer is a non-biological polymer, and wherein the nanomaterial is a metal nanoparticle, a semiconductor nanoparticle, an oxide nanoparticle, a magnetic nanoparticle, a carbon-based particle, a crystalline polymer, a biomaterial, a biomolecule, or a biological macromolecule,
 - providing a substrate surface, and
 - contacting the tip with the substrate surface, thereby transporting the ink from the nanoscopic tip to the substrate surface to form a structure on the substrate surface comprising both the polymer and the nanomaterial;
 - wherein the ink has an ink transport rate from the nanoscopic tip to the substrate which is increased by the use of the polymer ink carrier.
2. The method of claim 1, wherein the tip is one of a scanning probe microscopic tip, an atomic force microscopic tip, a non-hollow tip, or a hollow tip.
3. The method of claim 1, wherein the tip comprises an inorganic surface.
4. The method of claim 1, wherein a plurality of tips are provided comprising ink disposed at the end of the tip, and transporting the ink from the tips to the substrate surface forms a plurality of structures on the surface comprising both the polymer and the nanomaterial.
5. The method of claim 1, wherein the tip is heated to effect transport.
6. The method of claim 1, wherein the tip is disposed at the end of a cantilever.
7. The method of claim 1, wherein the nanomaterial comprises a nanoparticle comprising an average particle size of 2 nm to 100 nm or 2 nm to 25 nm.

8. The method of claim 1, wherein the nanomaterial comprises a spherical material or an elongated material.
9. The method of claim 1, wherein the nanomaterial comprises a metal nanoparticle, a magnetic nanoparticle, a fullerene nanoparticle, a carbon nanotube a nanowire, a nanorod, or a quantum dot.
10. The method of claim 1, wherein the nanomaterial comprises at least one biological macromolecule, at least one biomolecule, at least one protein, at least one antibody, or at least one crystallized conducting polymer.
11. The method of claim 1, wherein the polymer is one of a linear polymer, and a polymer soluble in water and organic solvent.
12. The method of claim 1, wherein the polymer is one of a poly(alkylene oxide) or a poly(alkylene imine), or a polyethylene oxide, wherein the polyethylene oxide has a molecular weight of more than 50,000.
13. The method of claim 1, wherein the ink consists essentially of the polymer and the nanomaterial.
14. The method of claim 1, wherein the ink further comprises a solvent for the polymer.
15. The method of claim 1, wherein the substrate surface is a semiconductor or metal substrate surface.
16. The method of claim 1, wherein the substrate surface comprises a nanoelectrodes gap.
17. The method of claim 1, wherein the transporting is carried out with at least 40% relative humidity, or at least 70% relative humidity.

18. The method of claim 1, wherein the structure has a lateral dimension of 1 micron or less or of 100 nm or less.
19. The method of claim 1, wherein the structure is a dot or a line.
20. The method of claim 1, wherein the structure has a height of at least 10 nm.
21. The method of claim 1, wherein method is repeated to provide a plurality of structures on the surface.
22. The method of claim 1, wherein method is repeated to provide a plurality of structures on the surface which are separated from each other by less than a micron.
23. The method of claim 1, wherein the step of transporting is carried out by contacting the tip with the surface and holding the tip stationary.
24. The method of claim 1, wherein the step of transporting is carried out by contacting the tip with the surface and moving the tip with respect to the surface, or moving the surface with respect to the tip.
25. The method of claim 1, wherein the step of transporting is carried out in a tapping mode.
26. The method of claim 1, further comprising the step of removing at least some of the polymer from the structure.
27. The method of claim 1, wherein the tip is a nanoscopic tip, the polymer is a soluble polymer, and the nanomaterial is a nanoparticle.
28. The method of claim 1, wherein the tip is a scanning probe tip, the polymer is a synthetic polymer, and the nanomaterial is a nanoparticle, a protein, or an antibody.

29. The method of claim 1, wherein the tip is an AFM tip, the polymer is a polyethylene oxide, polyethylene glycol, or polyethylene imine, and the nanomaterial is a nanoparticle or a biological material.

30. A method comprising:
providing an elastomeric, patterned, nanoscopic stamp,
providing an ink disposed on a surface of the stamp, wherein the ink comprises at least one nanomaterial and at least one polymer as an ink carrier of the nanomaterial, wherein the at least one polymer is a non-biological polymer, and wherein the nanomaterial is a metal nanoparticle, a semiconductor nanoparticle, an oxide nanoparticle, a magnetic nanoparticle, a carbon-based particle, a crystalline polymer, a biomaterial, a biomolecule, or a biological macromolecule,
providing a substrate surface, and
transporting the ink from the stamp to the substrate surface to form a structure on the surface comprising both the polymer and the nanomaterial;
wherein the ink has an ink transport rate from the nanoscopic tip to the substrate which is increased by the use of the polymer ink carrier.

31. A method comprising:
(A) providing one of a nanoscopic tip or a nanoscopic stamp;
(B) providing a mixture comprising an ink and a carrier matrix, wherein the carrier matrix is selected from a) polyalkylene oxides having a molecular weight of more than 50,000 and b) polyalkylene imines;
(C) disposing the mixture at one of the tip or the stamp;
(D) providing a substrate surface; and
(E) transporting the mixture from one of the tip or the stamp to the substrate surface to form a pattern on the substrate surface,
wherein the ink has an ink transport rate to the substrate which is increased by the use of the polymer ink carrier.

32. The method of claim 31, wherein the one of the tip or the stamp is a tip.

33. The method of claim 32, wherein the tip is one of a scanning probe microscopic tip, and an atomic force microscopic tip.

34. The method of claim 31, wherein the step of disposing the mixture comprises immersing the tip in the mixture.
35. The method of claim 31, wherein the step of disposing the mixture comprises immersing the tip in the mixture and drying the mixture.
36. The method of claim 31, wherein the one of the tip or the stamp is a microcontact printing stamp.
37. The method of claim 31, wherein the ink is a hard ink and the hard ink is selected from the group consisting of nanoparticles, carbon based materials and crystallized polymers.
38. The method of claim 31, wherein the ink is a hard ink and the hard ink is selected from the group of metal nanoparticles, magnetic nanoparticles and fullerenes.
39. The method of claim 31, wherein the ink comprises at least one biomolecule.
40. The method of claim 39, wherein the biomolecule is selected from the group consisting of nucleic acids, peptides and proteins.
41. The method of claim 31, wherein the ink comprises at least one protein.
42. The method of claim 41, wherein the at least one protein is an antibody.
43. The method of claim 31, wherein the polymer is polyethylene oxide.
44. A method comprising
(A) providing a tip or a stamp;
(B) providing a mixture comprising a nanomaterial and a carrier matrix comprising at least one non-biological polymer as an ink carrier of the nanomaterial, and wherein the nanomaterial is a metal nanoparticle, a semiconductor nanoparticle,

an oxide nanoparticle, a magnetic nanoparticle, a carbon-based particle, a crystalline polymer, a biomaterial, a biomolecule, or a biological macromolecule;

(C) disposing the mixture on the tip or stamp;

(D) providing a substrate surface; and

(E) transporting the mixture from the tip or stamp to the substrate surface to form a pattern on the substrate surface such that the pattern comprising both the carrier matrix and the nanomaterial;

wherein the ink has an ink transport rate from the nanoscopic tip to the substrate which is increased by the use of the polymer ink carrier.

45. The method of claim 44, wherein the nanomaterial comprises at least one biomolecule, and the carrier matrix comprises a material selected from the group consisting of polyalkylene oxides and polyalkylene imines.

46. The method of claim 1, wherein the nanoscopic tip is part of a larger structure comprising a plurality of nanoscopic tips with inks disposed at the ends of the nanoscopic tips, wherein the inks comprise multiple one of biomolecules and multiple proteins, which are simultaneously transported from the nanoscopic tips to the substrate.

47. The method of claim 1, wherein the nanoscopic tip is part of a larger structure comprising a plurality of nanoscopic tips with inks disposed at the ends of the nanoscopic tips, wherein the inks comprise multiple biomolecules which are simultaneously transported from the nanoscopic tips to the substrate to form dots which have an average dot diameter characterized by less than 7% variation.

48. The method of claim 1, wherein the nanoscopic tip is part of a larger structure comprising a plurality of nanoscopic tips with inks disposed at the ends of the nanoscopic tips, wherein the inks comprise multiple proteins which are simultaneously transported from the nanoscopic tips to the substrate to form dots which have an average dot diameter characterized by less than 7% variation.