

CLAIMS

1. An array, comprising:
a plurality of polymers disposed on a substrate, the polymers each comprising one or more polymerized monomers and one or more photoinitiators, or one or more photocleavage products thereof.
2. The array of claim 1, wherein the one or more photoinitiators include at least one of: 2,2-Dimethoxy-2-phenylacetophenone (DMPA), 1-hydroxycyclohexyl phenyl ketone (HCPK), or 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP).
3. The array of claim 1 or 2, wherein the one or more photoinitiators were exposed to the UV light concurrently with a plurality of monomers thereby polymerizing the monomers into a polymer comprising the initiator and/or the photocleavage product of the initiator.
4. The array of any one of claims 1-3, wherein the one or more photocleavage products include one or both of a benzoyl and a ketal fragment.
5. The array of claim 4, wherein the one or more photocleavage products are benzil or benzoin, or each polymer further comprising a reaction product of the one or more photocleavage products.
6. The array of any one of claims 1-5, wherein the monomers were polymerized via application of ultraviolet (UV) light.

7. The array of claim 6, wherein the application of UV light was for between about 5 minutes and about 60 minutes.
8. The array of claim 7, wherein the application of UV light was for about 20 minutes.
9. The array of any one of claims 6-8, wherein the UV light was at a wavelength of between about 250 nm and about 400 nm.
10. The array of any one of claims 1-9, wherein the array of polymers includes polymer spots each including a concentration of the photoinitiator between about 0.5x (6.25 mM) and about 4x (50 mM).
11. The array of any one of claims 1-9, wherein the concentration of photoinitiator is about 1x (12.5 mM).
12. The array of any one of claims 1-11, wherein one or more of the monomers is selected from the group consisting of acrylamide, 2-carboxyethyl acrylate, acrylic acid, 2-cyanoethyl acrylate, N-[tris(hydroxymethyl)methyl] acrylamide, hydroxypropyl acrylate isomers, 4-hydroxybutyl acrylate, N-hydroxyethyl acrylamide, N,N-dimethylacrylamide, N-isopropylacrylamide, N-(1,1-dimethyl-3-oxobutyl) acrylamide, 2-methacryloxyethyl phenyl urethane, 1-acryloyloxy-3-(methacryloyloxy)-2-propanol and ethylene glycol phenyl ether acrylate.
13. The array of any one of claims 1-11, wherein one or more of the monomers is selected from the group consisting of 2-carboxyethyl acrylate, acrylic acid, acrylamide, histamine acrylate, N-[tris(hydroxymethyl)methyl]acrylamide, hydroxypropyl acrylate isomers, 4-

hydroxybutyl acrylate, N-hydroxyethyl acrylamide, N,N,-dimethylacrylamide, N-(1,1-dimethyl-3-oxobutyl)acrylamide, N-isopropylacrylamide, ethylene glycol phenyl ether acrylate, N,N'-methylenebisacrylamide, 1,1,3,3,3-Hexafluoroisopropyl acrylate, and N-*tert*-octylacrylamide.

14. The array of any one of claims 1-13, wherein each polymer on the array is a homopolymer comprising only one monomer; each polymer on the array is a heteropolymer comprising at least two monomers; or one or more polymers on the array are homopolymers comprising only one monomer and one or more polymers on the array are heteropolymers comprising at least two monomers.

15. The array of any one of claims 1-13, comprising one or more heteropolymer comprising at least three monomers.

16. The array of any one of claims 1-15, wherein each polymer on the array comprises one or more monomers selected from the group consisting of:

a. acrylamide, 2-carboxyethyl acrylate, acrylic acid, 2-cyanoethyl acrylate, N-[tris(hydroxymethyl)methyl] acrylamide, hydroxypropyl acrylate isomers, 4-hydroxybutyl acrylate, N-hydroxyethyl acrylamide, N,N-dimethylacrylamide, N-isopropylacrylamide, N-(1,1-dimethyl-3-oxobutyl) acrylamide, 2-methacryloxyethyl phenyl urethane, 1-acryloyloxy-3-(methacryloyloxy)-2-propanol and ethylene glycol phenyl ether acrylate; or

b. 2-carboxyethyl acrylate, acrylic acid, acrylamide, histamine acrylate, N-[tris(hydroxymethyl)methyl]acrylamide, hydroxypropyl acrylate isomers, 4-hydroxybutyl acrylate, N-hydroxyethyl acrylamide, N,N,-dimethylacrylamide, N-(1,1-dimethyl-3-

oxobutyl)acrylamide, N-isopropylacrylamide, ethylene glycol phenyl ether acrylate, N,N'-methylenebisacrylamide, 1,1,3,3,3-Hexafluoroisopropyl acrylate, and N-*tert*-octylacrylamide.

17. The array of any one of the preceding claims, wherein the substrate comprises a surface that is functionalized.
18. The array of claim 17, wherein the surface is functionalized with a silane or siloxane coating.
19. The array of claim 18, wherein the surface is functionalized with an acrylosiloxane.
20. The array of claim 19, wherein the acrylosiloxane is selected from 3-methacryloxypropyl trimethoxy silane, 3-acryloxypropyl trimethoxy silane, N-(3-acryloxy-2-hydroxypropyl-3-aminopropyltriethoxysilane, 3-methacryloxy propyldimethylchlorosilane, and a combination thereof.
21. The array of any one of the preceding claims, wherein the polymers are covalently attached to the substrate.
22. The array of any one of claims 17-21, wherein the polymers are covalently attached to the surface by directly polymerizing the monomers with the functionalization on the surface.
23. The array of claim 22, wherein the polymerization occurs on the surface of the substrate in the presence of the photoinitiator.

24. The array of any one of the preceding claims, wherein the array does not degrade detectably after heating for about 5 minutes at temperatures as high as 250 degrees Celsius.
25. The array of any one of the preceding claims, wherein the array does not degrade detectably after heating for from about 5 minutes to about 20 minutes at temperatures as high as 400 degrees Celsius.
26. The array of claim 1, wherein:
the photoinitiator is DMPA at about 1x (12.5 mM);
the polymers comprise one or more monomers selected from the group consisting of acrylamide, 2-carboxyethyl acrylate, acrylic acid, 2-cyanoethyl acrylate, N-[tris(hydroxymethyl)methyl] acrylamide, hydroxypropyl acrylate isomers, 4-hydroxybutyl acrylate, N-hydroxyethyl acrylamide, N,N-dimethylacrylamide, N-isopropylacrylamide, N-(1,1-dimethyl-3-oxobutyl) acrylamide, 2-methacryloxyethyl phenyl urethane, 1-acryloyloxy-3-(methacryloyloxy)-2-propanol and ethylene glycol phenyl ether acrylate; and
the polymers and DMPA were exposed to UV light having a wavelength of between about 250 nm and about 400 nm for about 20 minutes after the polymers and DMPA were deposited on a surface of the substrate.
27. The array of any one of the preceding claims, wherein the array of polymers includes between about 14 and about 70 hydrogel spots.
28. A method for detecting an unlabeled analyte, comprising:

contacting one or more samples including one or more unlabeled analytes with an array of polymers comprised on a substrate, the polymers including a photoinitiator that was previously exposed to ultraviolet (UV) light for a first predetermined period of time;

incubating the one or more samples disposed on the array of polymers for a second predetermined period of time;

heating the array of polymers at a predetermined temperature for a third predetermined period of time; and

measuring, using an imaging device, an amount of one or more colorimetric or luminescence signals produced in response to the heating.

29. The method of claim 28, wherein the photoinitiator includes at least one of: 2,2-Dimethoxy-2-phenylacetophenone (DMPA), 1-hydroxycyclohexyl phenyl ketone (HCPK), or 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP).

30. The method of claim 28, wherein the photoinitiator was exposed to the UV light concurrently with a plurality of monomers thereby polymerizing the monomers into a polymer comprising the initiator and/or a photocleavage product of the initiator.

31. The method of claim 30, wherein the photocleavage product includes one or both of a benzoyl and a ketal fragment.

32. The method of claim 31, wherein the photocleavage product is benzil or benzoin, or the polymer further comprises a reaction product of the photocleavage product.

33. The method of claim 28, wherein the first predetermined period of time is between about 5 minutes and about 60 minutes.
34. The method of claim 33, wherein the first predetermined period of time is about 20 minutes.
35. The method of claim 28, wherein the UV light has a wavelength of between about 250 nm and about 400 nm.
36. The method of claim 28, wherein the array of polymers includes polymer spots each including a concentration of the photoinitiator between about 0.5x (6.25 mM) and about 4x (50 mM).
37. The method of claim 36, wherein the concentration of photoinitiator is about 1x (12.5mM).
38. The method of claim 28, wherein the third predetermined period of time is about 5 minutes.
39. The method of claim 28, wherein the predetermined temperature is between about 100 degrees Celsius and about 400 degrees Celsius.
40. The method of claim 39, wherein the predetermined temperature is about 250 degrees Celsius.

41. The method of claim 28, wherein the second predetermined period of time is between about 10 and about 15 minutes.
42. The method of claim 28, wherein:
the photoinitiator is DMPA,
the array of polymers including DMPA that was previously exposed to UV light having a wavelength of between about 250 nm and about 400 nm for about 20 minutes, and
the heating the array of polymers includes heating the array of polymers at about 250 degrees Celsius for about 5 minutes.
43. The method of claim 42, wherein the one or more samples includes one or more urine samples.
44. The method of claim 28, wherein the array of polymers includes between about 14 and about 70 hydrogel spots.
45. A method, comprising:
preparing a photoinitiator solution including a photoinitiator;
preparing a plurality of monomer stock solutions each including a monomer;
adding a volume of the photoinitiator solution to a volume of each of the plurality of monomer stock solutions and each of a plurality of combinations of the plurality of monomer stock solutions to produce a plurality of spotting solutions;
spotting a predetermined volume of each of the plurality of spotting solutions onto a surface; and

exposing the array comprising the spotting solutions to ultraviolet (UV) light for a predetermined period of time;

thereby polymerizing the predetermined volume of each of the plurality of spotting solutions spotted onto the surface to produce an array of polymers.

46. The method of claim 45, wherein the preparing the solution includes:

dissolving an amount of the photoinitiator in a first volume of dimethyl sulfoxide (DMSO) to produce a stock solution; and

adding to the stock solution at least one of: a volume of mineral oil, a volume of water, a volume of glycerol, or a second volume of DMSO.

47. The method of claim 45, wherein the predetermined period of time is about 60 minutes.

48. The method of claim 45, wherein the UV light has a wavelength of between about 250 nm and about 400 nm.

49. The method of claim 45, wherein the polymerizing the predetermined volume of each of the plurality of spotting solutions spotted onto the surface includes exposing the predetermined volume of each of the plurality of spotting solutions spotted onto the surface to UV light for a predetermined period of time, such that the UV light catalyzes curing of one or more monomers in the spotting solutions and covalent attachment of the one or more monomers to the surface.

50. The method of claim 45, wherein the photoinitiator includes at least one of: 2,2-Dimethoxy-2-phenylacetophenone (DMPA), 1-hydroxycyclohexyl phenyl ketone (HCPK), or 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP).

51. A method, comprising:

receiving, at a processor and for a plurality of subjects, image data associated with colorimetric or luminescence signal profiles of a plurality of array spots (1) contacted with one or more samples associated with that subject and (2) heated at a predetermined temperature for a predetermined period of time, each of the plurality of array spots including a different hydrogel composition with a photoinitiator that was previously exposed to ultraviolet (UV) light;

processing, for each of the plurality of subjects, the image data associated with that subject to produce color intensity values for each of the plurality of array spots;

training, for each of the plurality of subjects, a neural network to classify that subject by calibrating the neural network using the color intensity values associated with each subject other than that subject and of the plurality of subjects; and

predicting, for each of the plurality of subjects, a diagnostic class for that subject using the neural network trained for that subject.

52. The method of claim 51, wherein the processing the image data to produce the color intensity values for each of the plurality of array spots includes summing red, green, and blue pixel intensities for each of the plurality of array spots.

53. The method of claim 51, wherein the neural network is a multilayer perceptron.

54. The method of claim 53, wherein the multilayer perceptron includes an input layer having about 210 nodes and a hidden layer having between about 30 nodes to 250 nodes.
55. The method of claim 51, wherein the neural network uses a rectifier as an activation function and performs logistic regression using a limited-memory Broyden–Fletcher–Goldfarb–Shanno (L-BFGS) algorithm.
56. The method of claim 51, wherein the diagnostic class is selected from a plurality of diagnostic classes including a healthy class and at least one cancer class.
57. The method of claim 51, wherein the diagnostic class is selected from a plurality of diagnostic classes including a healthy class, a plurality of cancer classes, and a Hepatitis B virus-infected class.
58. A method of determining disease, disorder, or condition state in a subject, comprising:
contacting an array of any of claims 1-27 with one or more analytes from the subject;
incubating the one or more analytes on the array for a first period of time, thereby allowing a portion of the one or more analytes to be captured on the array;
heating the array at a predetermined temperature for a second period of time; and
measuring, using an imaging device, an amount of one or more colorimetric or luminescence signals produced in response to the heating.
59. The method of claim 58, wherein contacting step comprises (a) contacting the array with one or more body samples of the subject; (b) contacting the array with at least one of blood, serum, plasma, urine, stool, saliva, bile, spinal fluid, interstitial

fluid, gastric juice, tears, solvent, and milk of the subject, in-vitro sample, or environmental sample; (c) contacting the array with one or more of plasma and urine of the subject; or (d) a combination of two or more of (a)-(c).

60. The method of claim 58 or 59, further comprising obtaining the one or more analytes from the subject or from a sample obtained from the subject.

61. The method of any one of claims 58-60, further comprising obtaining, based on the measuring, one or more images of the array or one or more representations thereof.

62. The method of any one of claims 58-61, wherein the second period of time is about 5 minutes.

63. The method of any one of claims 58-62, wherein the predetermined temperature is between about 100 degrees Celsius and about 400 degrees Celsius.

64. The method of any one of claims 58-62, wherein the predetermined temperature is about 250 degrees Celsius.

65. The method of any one of claims 58-64, wherein the one or more samples includes one or more urine samples.

66. The method of any one of claims 58-65, wherein the determining is via a method of any one of claims 51-57.

67. The method of any one of claims 58-66, wherein the disease is cancer.

68. The method of any one of claims 58-66, wherein the disease is a virus.

69. The method of any one of claims 58-67, further comprising treating the subject with a therapy if the subject is determined to have a disease.

70. The method of claim 69, wherein the therapy comprises surgery, chemotherapy, immunotherapy, or a combination thereof.