

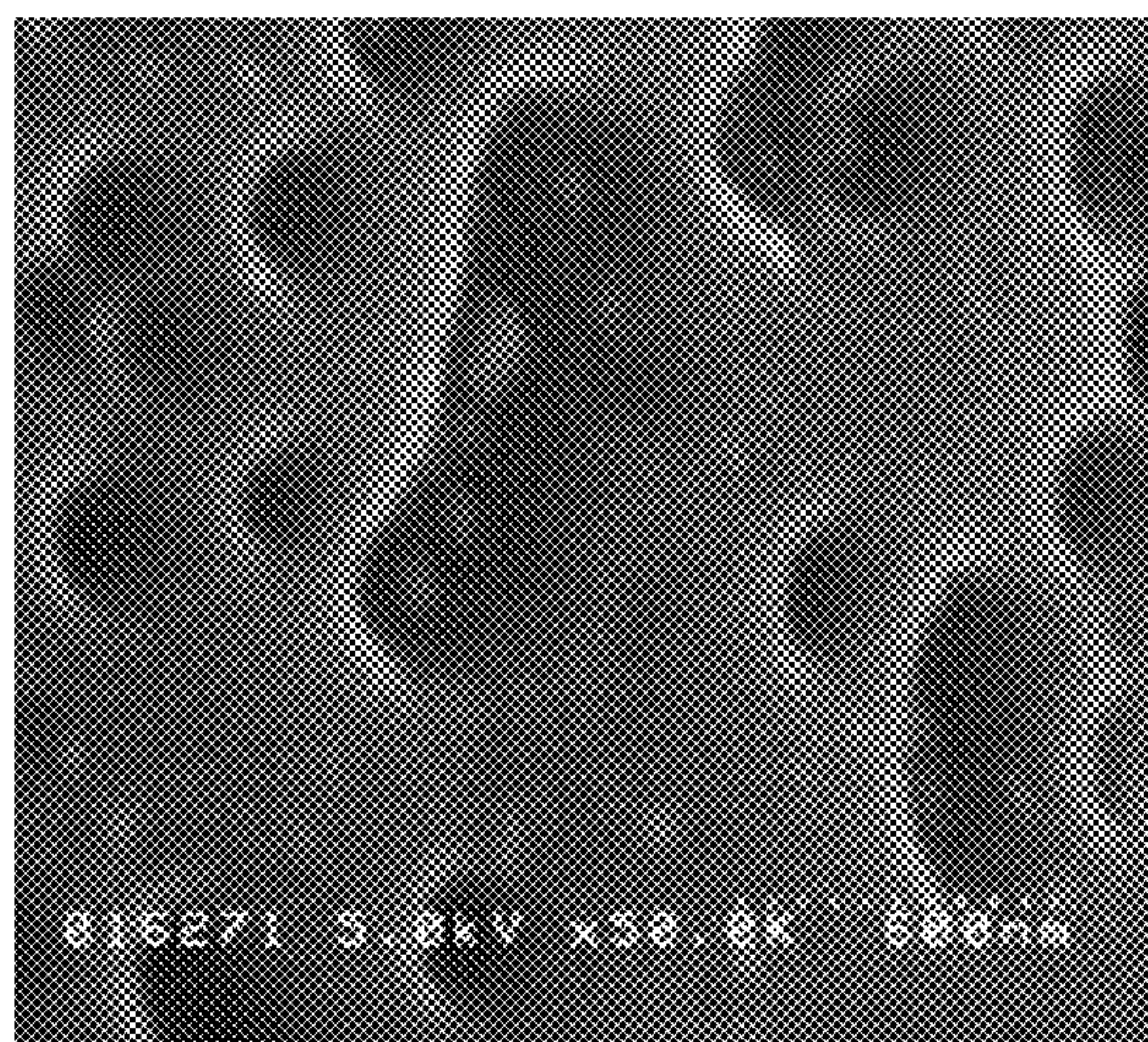
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(19) **United States**(12) **Patent Application Publication**
Istvan et al.(10) **Pub. No.: US 2010/0126870 A1**(43) **Pub. Date: May 27, 2010**(54) **CONTROLLED ELECTRODEPOSITION OF NANOPARTICLES**(52) **U.S. Cl. 205/96; 205/111; 205/555; 977/847**(76) **Inventors: Rudyard Lyle Istvan, Ft. Lauderdale, FL (US); Stephen M. Lipka, Nicholasville, KY (US)**

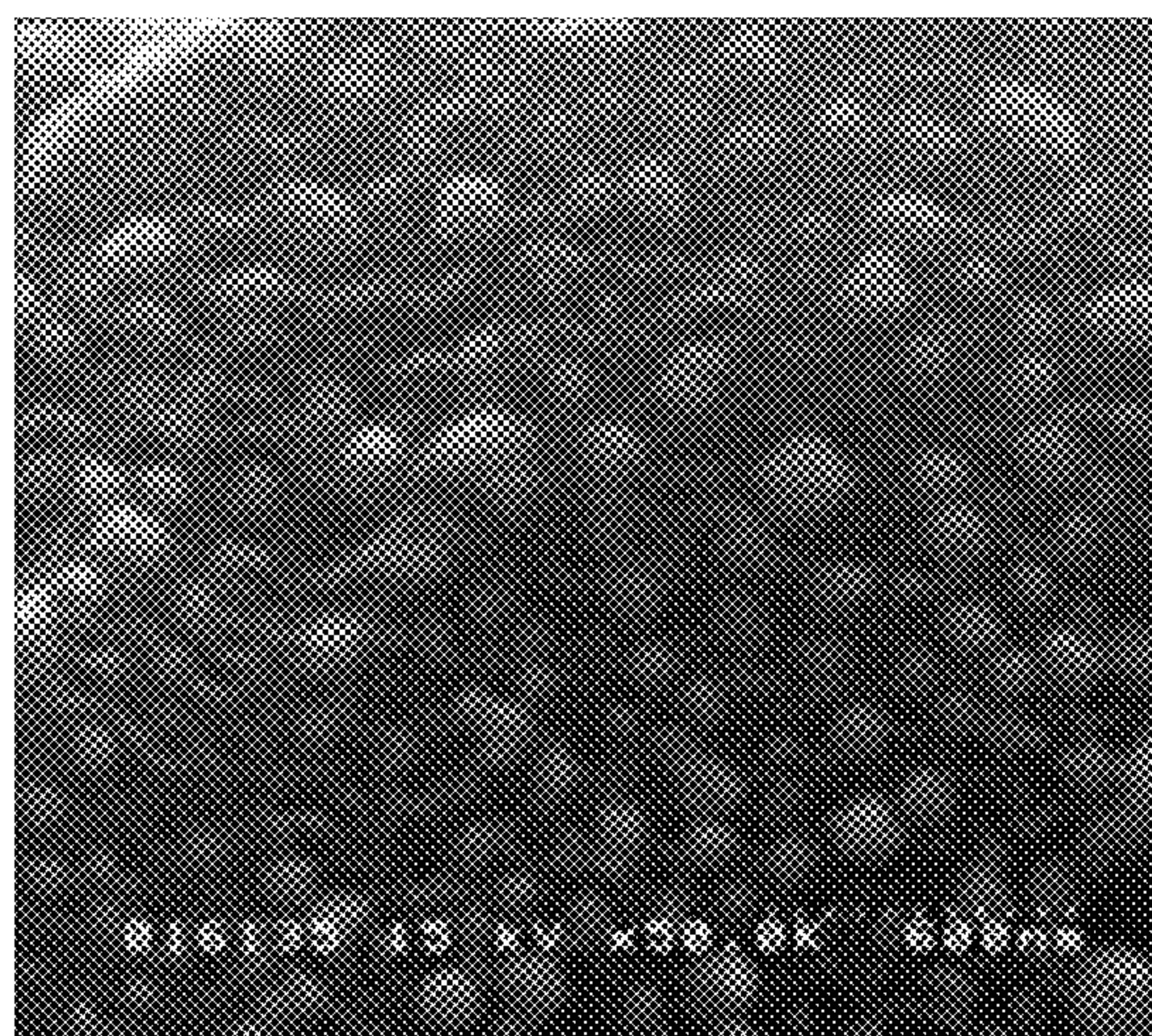
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C25D 5/18 (2006.01)
C25D 5/54 (2006.01)
C25B 1/00 (2006.01)(57) **ABSTRACT**

Deposition of nanoparticles onto carbon surfaces is described. Metal and/or metal oxide ions are deposited on a carbon surface by electrodeposition, such as by immersing a carbon and an anode in a salt bath, and applying a number of electrical pulses having a defined pulse width. The size, coverage density, and metallic composition of the nanoparticles may be affected by the pulse width of the electrical pulses, the number of electrical pulses, and the chemical composition of the salt bath, respectively. The carbon may be anodized before electrodeposition. If the carbon is a carbon precursor, after electrodeposition, the carbon precursor is carbonized to form a carbon. After electrodeposition, the carbon may be activated to form an activated carbon. The nanoparticles may serve as catalysts for activation rugosity of mesoporous carbons. The catalytically activated carbon materials may be used in all manner of devices that contain carbon materials.

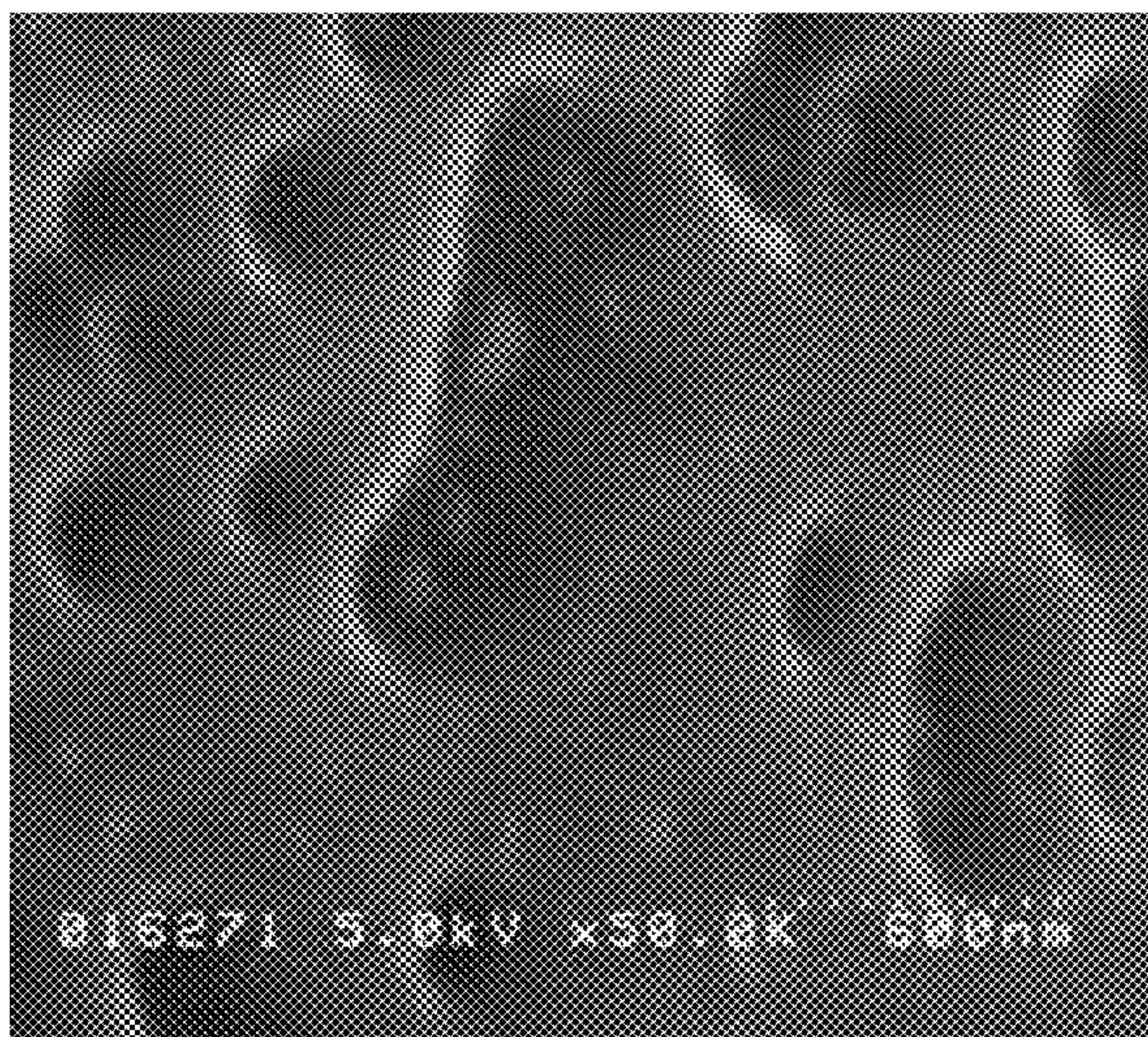
Variation in Nanoparticle Size and Coverage

0.25 wgt.% Ni(acac)₂ in THF
(3x) activated in 1:1 air:N₂ @
800°C for 7 minutes

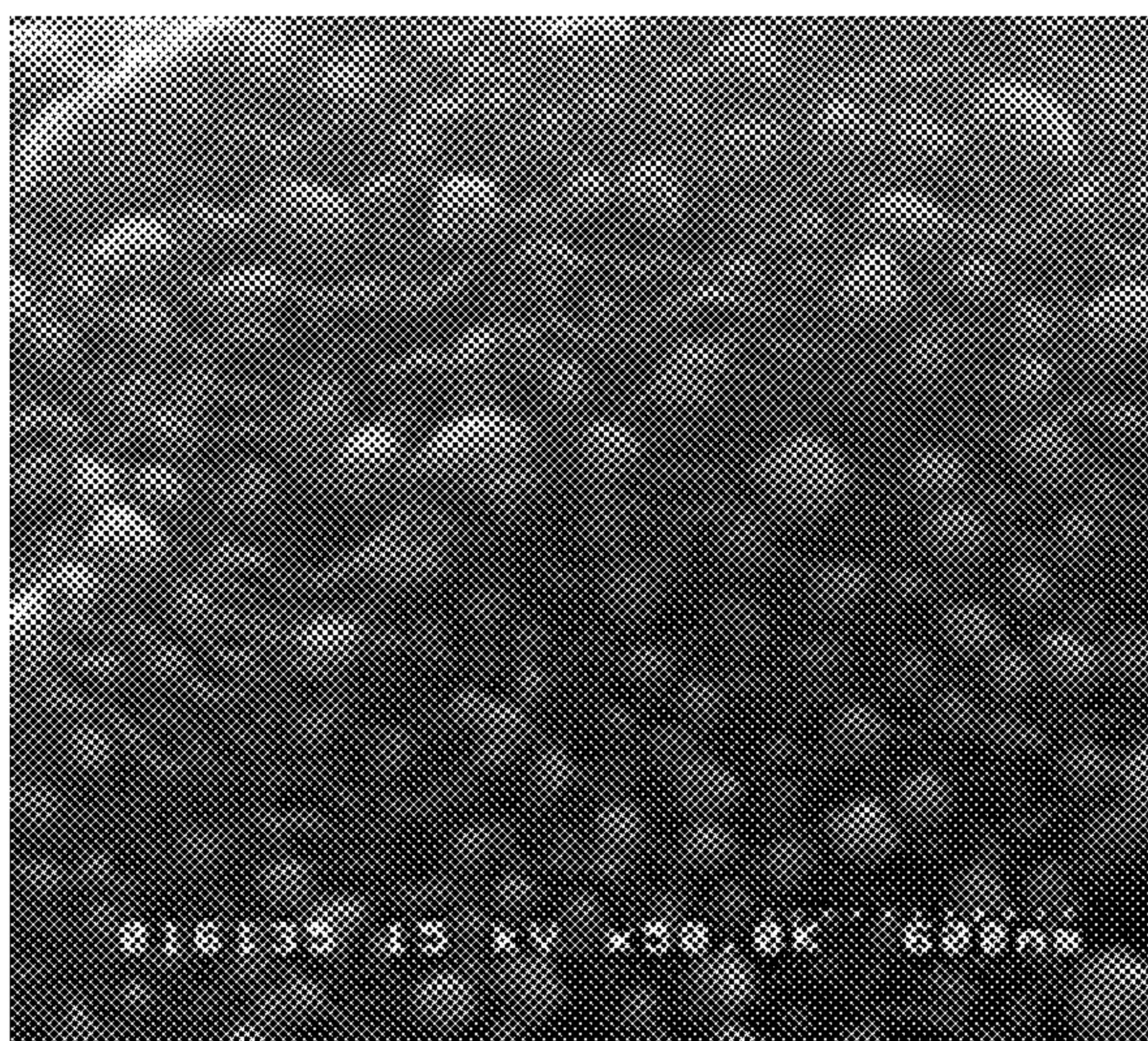


1.0 wgt.% Ni(acac)₂ in THF (2x)
calcined

Variation in Nanoparticle Size and Coverage

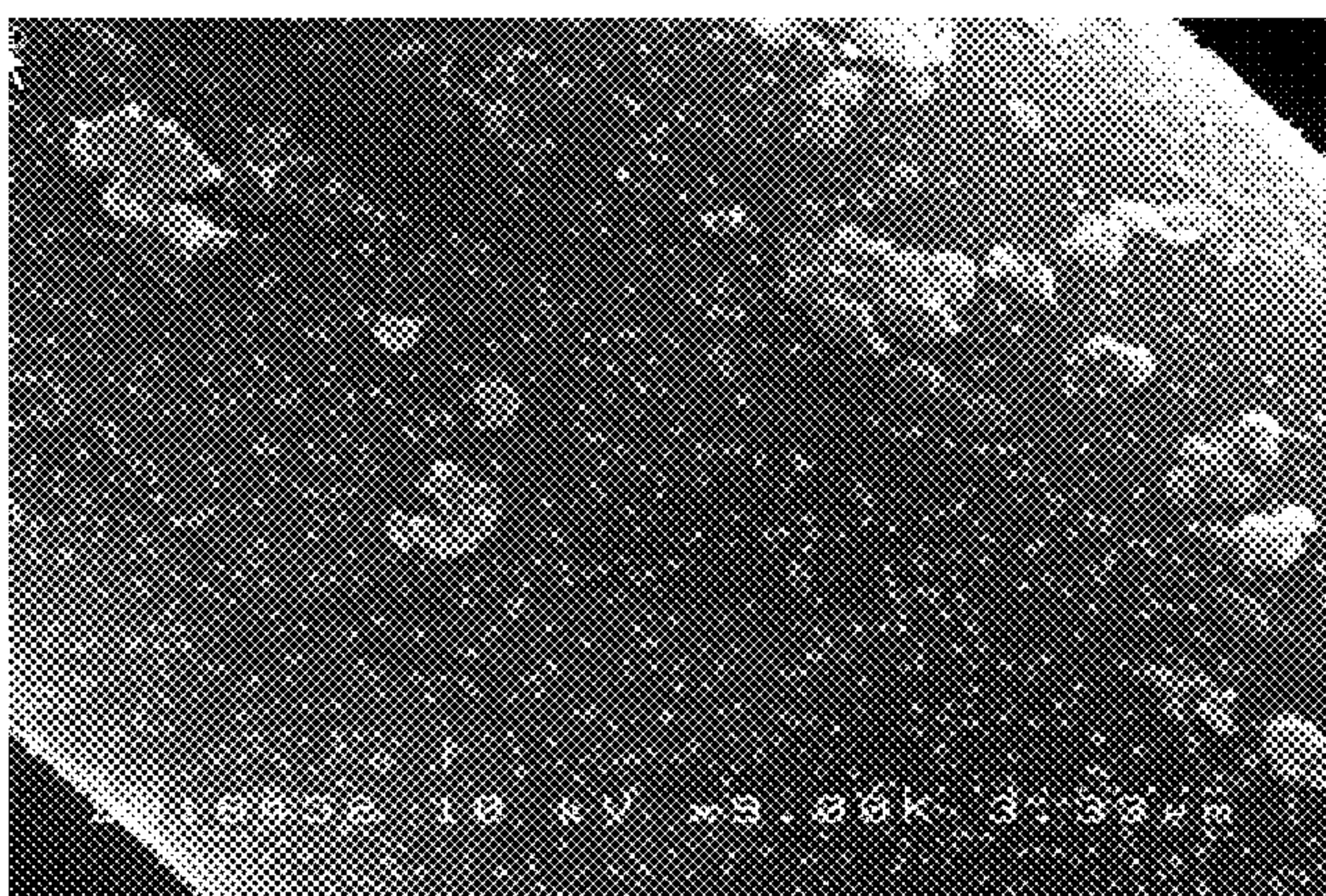


0.25 wgt.% Ni(acac)₂ in THF
(3x) activated in 1:1 air:N₂ @
800°C for 7 minutes

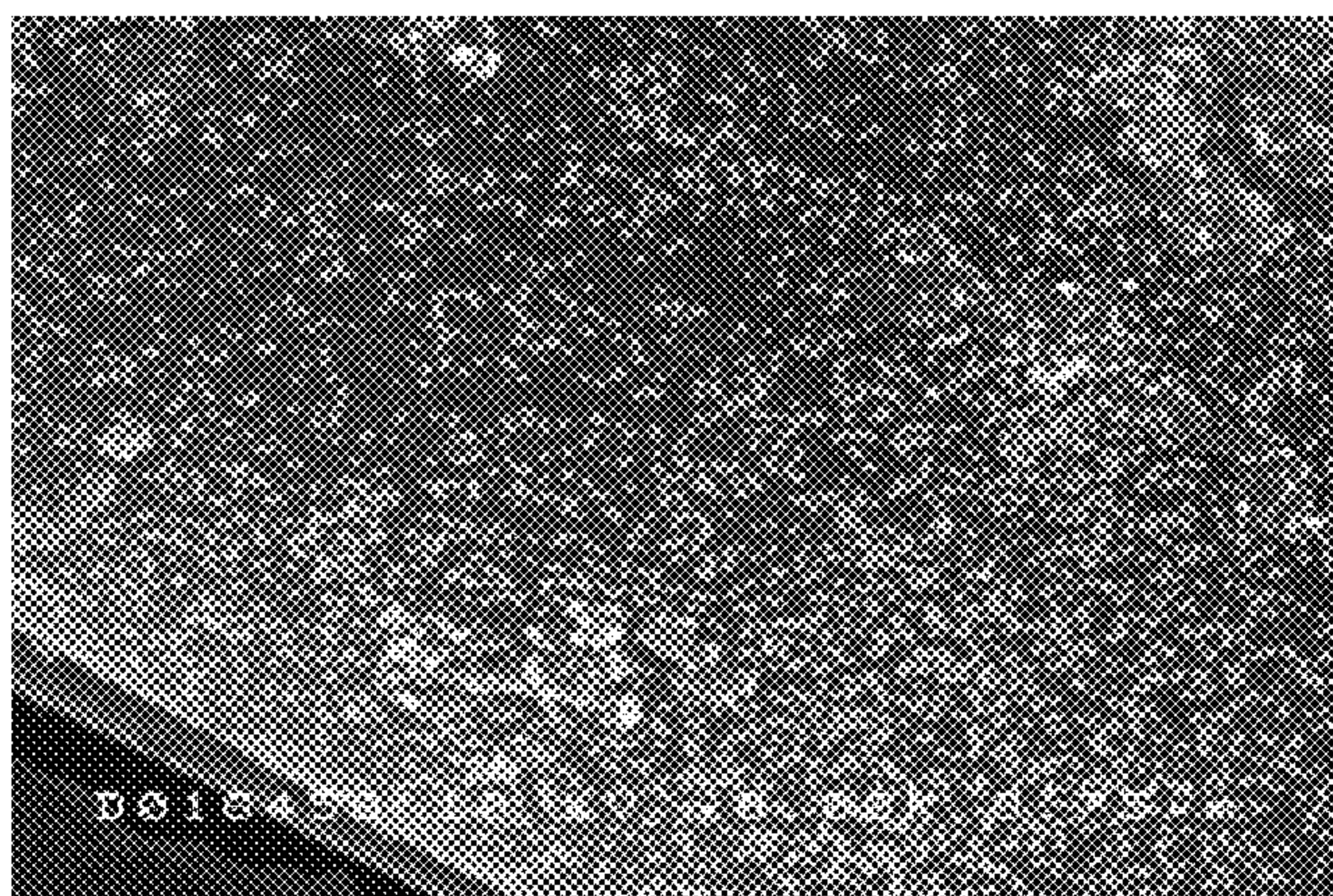


1.0 wgt.% Ni(acac)₂ in THF (2x)
calcined

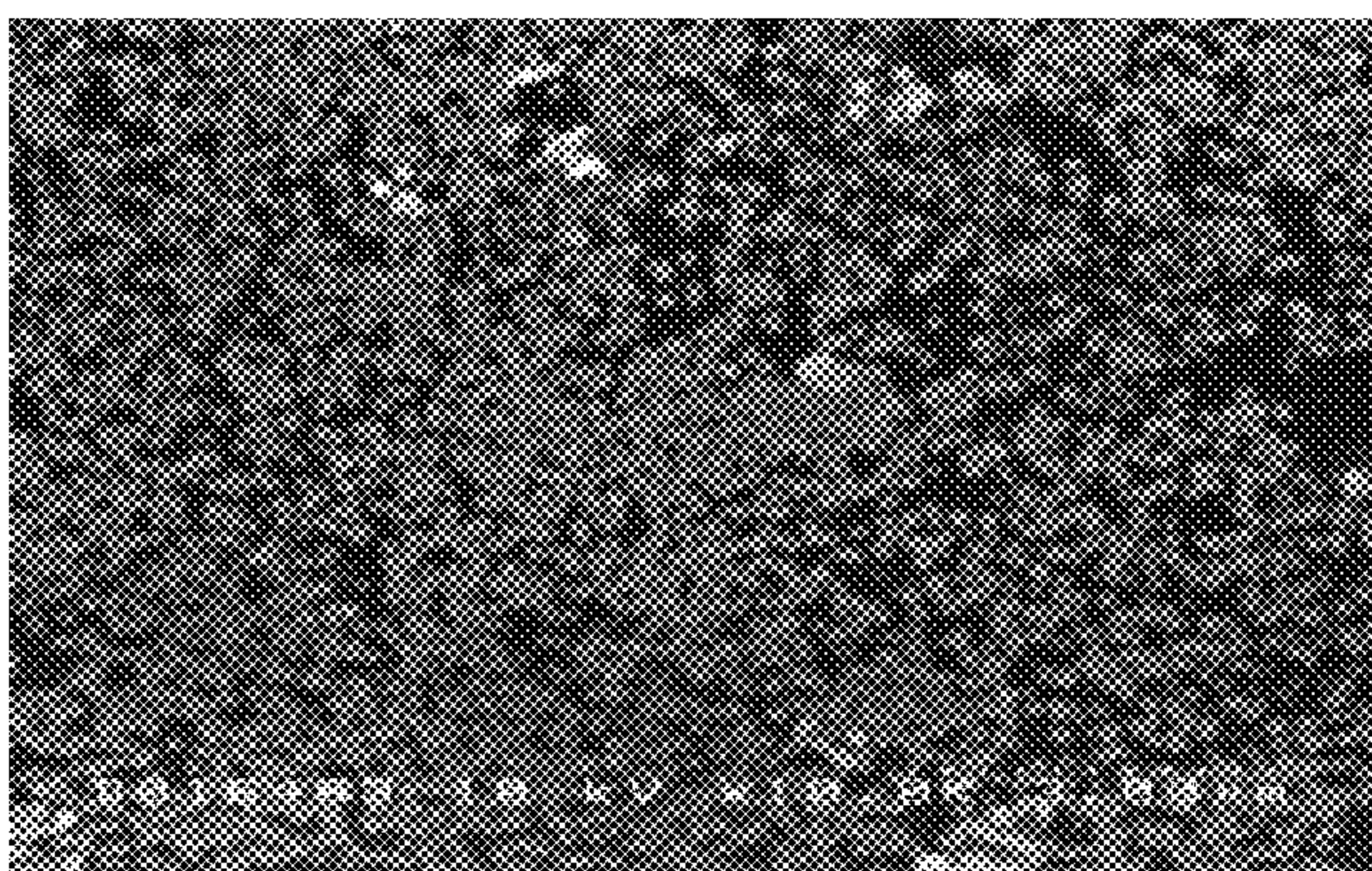
FIG. 1

Pulse Cycle Coverage Control

Electrodeposited Ni
1.18 V_{SCE} 1Hz (50% Duty Cycle)
10 Cycles



Electrodeposited Ni
1.18 V_{SCE} 1Hz (50% Duty Cycle)
30 Cycles

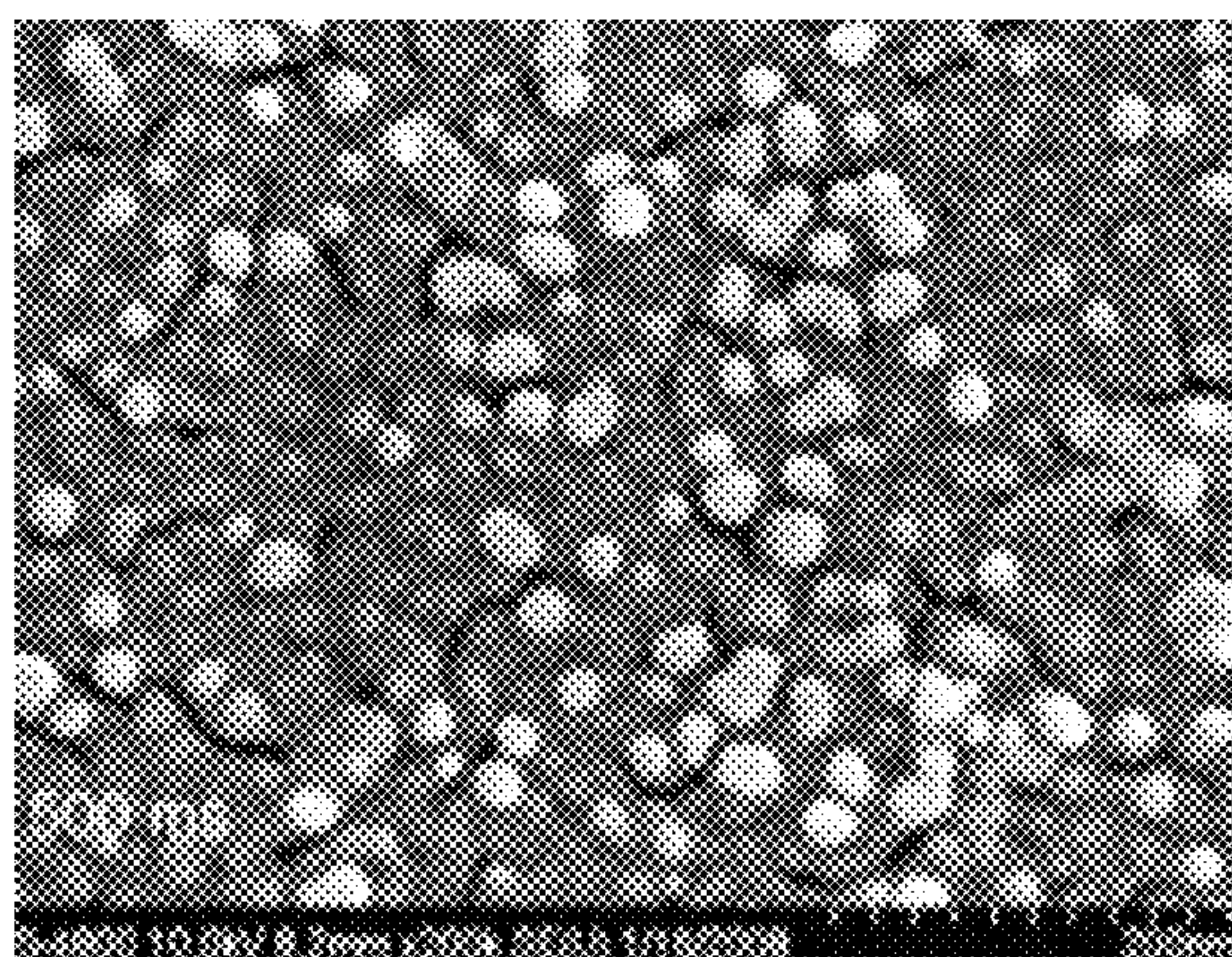


Electrodeposited Ni
1.18 V_{SCE} 1Hz (50% Duty Cycle)
60 Cycles

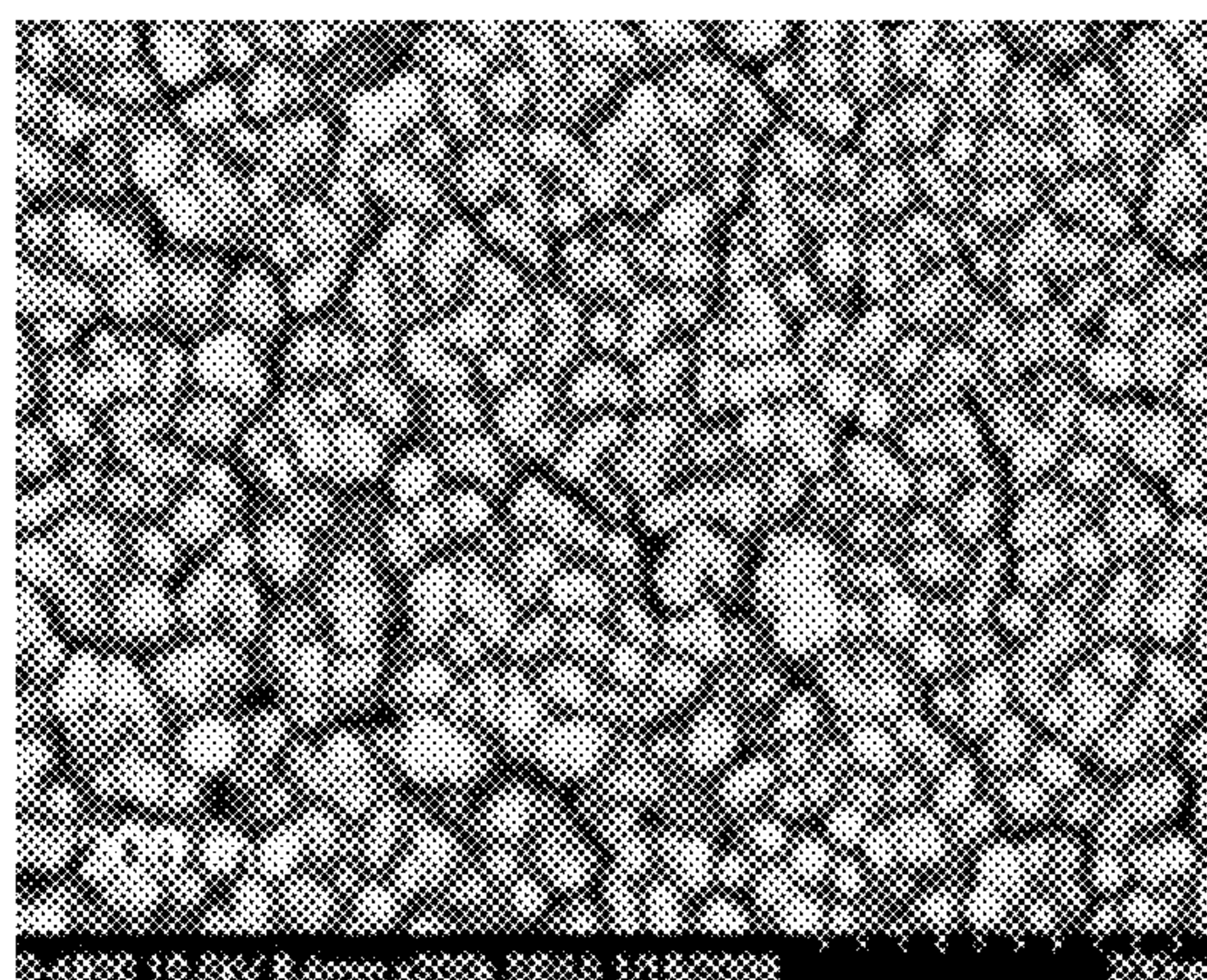
FIG. 2

Pulse Duration Size Control

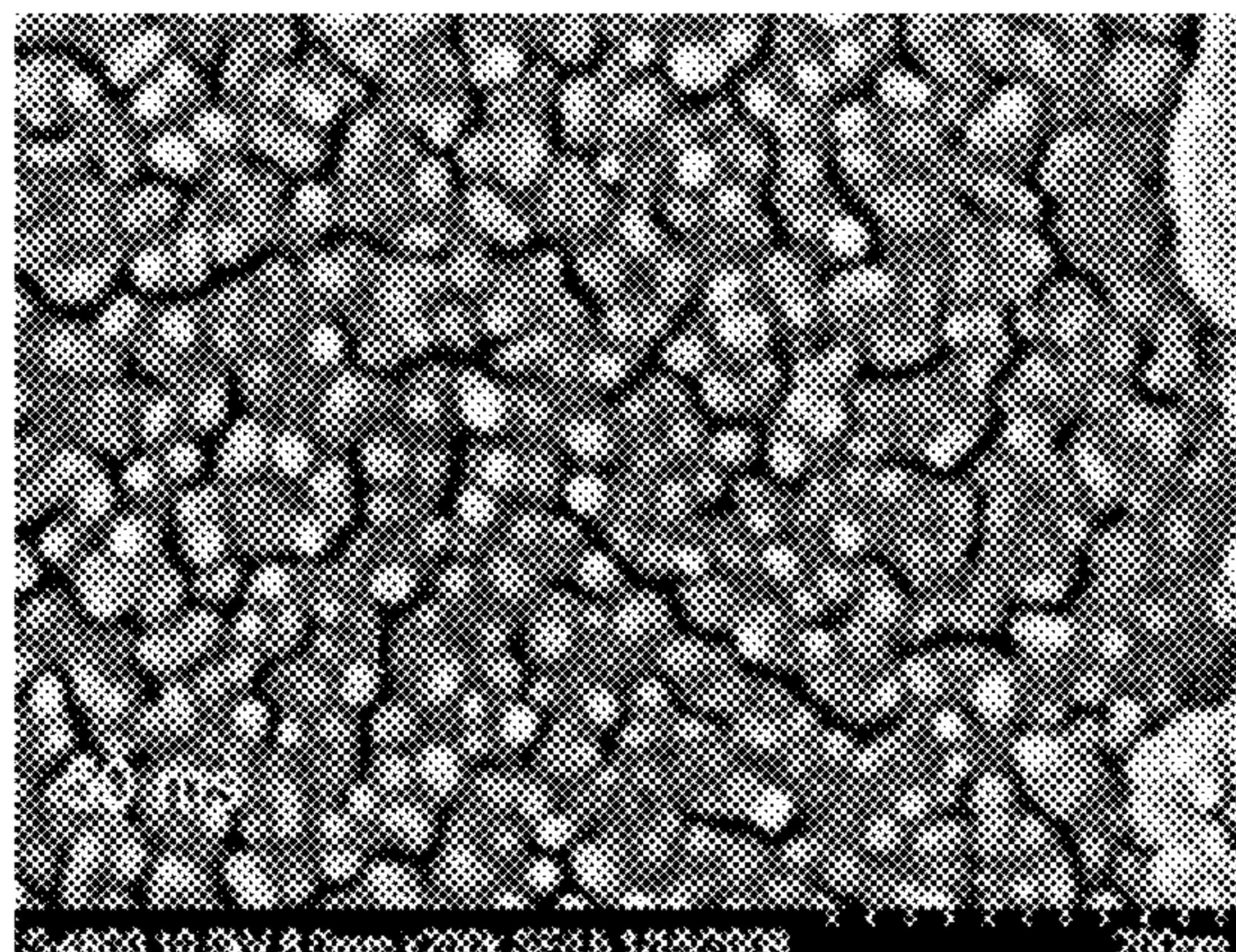
Electrodeposited Ni, 1.18 V_{SCE}, 10 Cycles, 1 second pulse "off" time



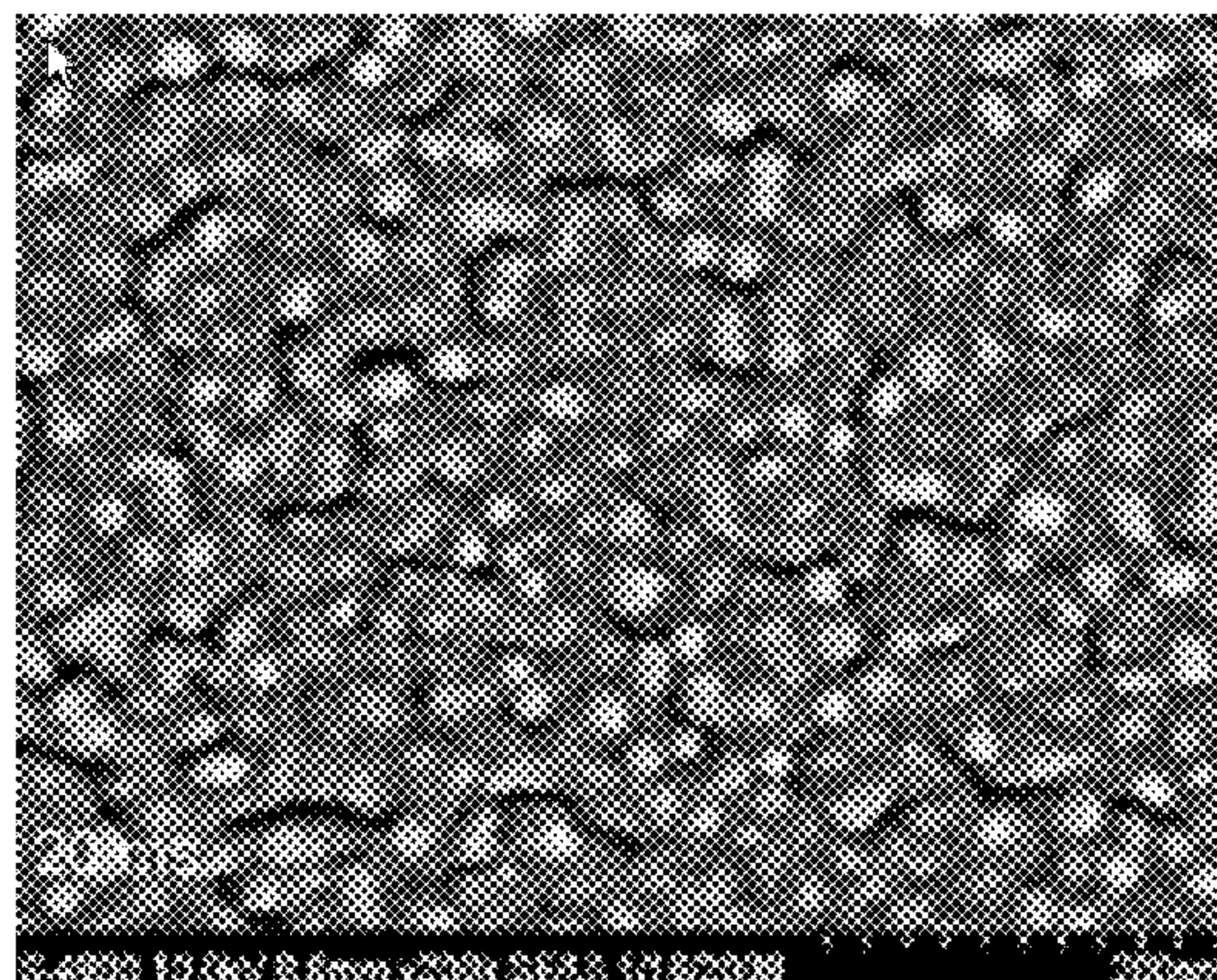
500 ms



200 ms



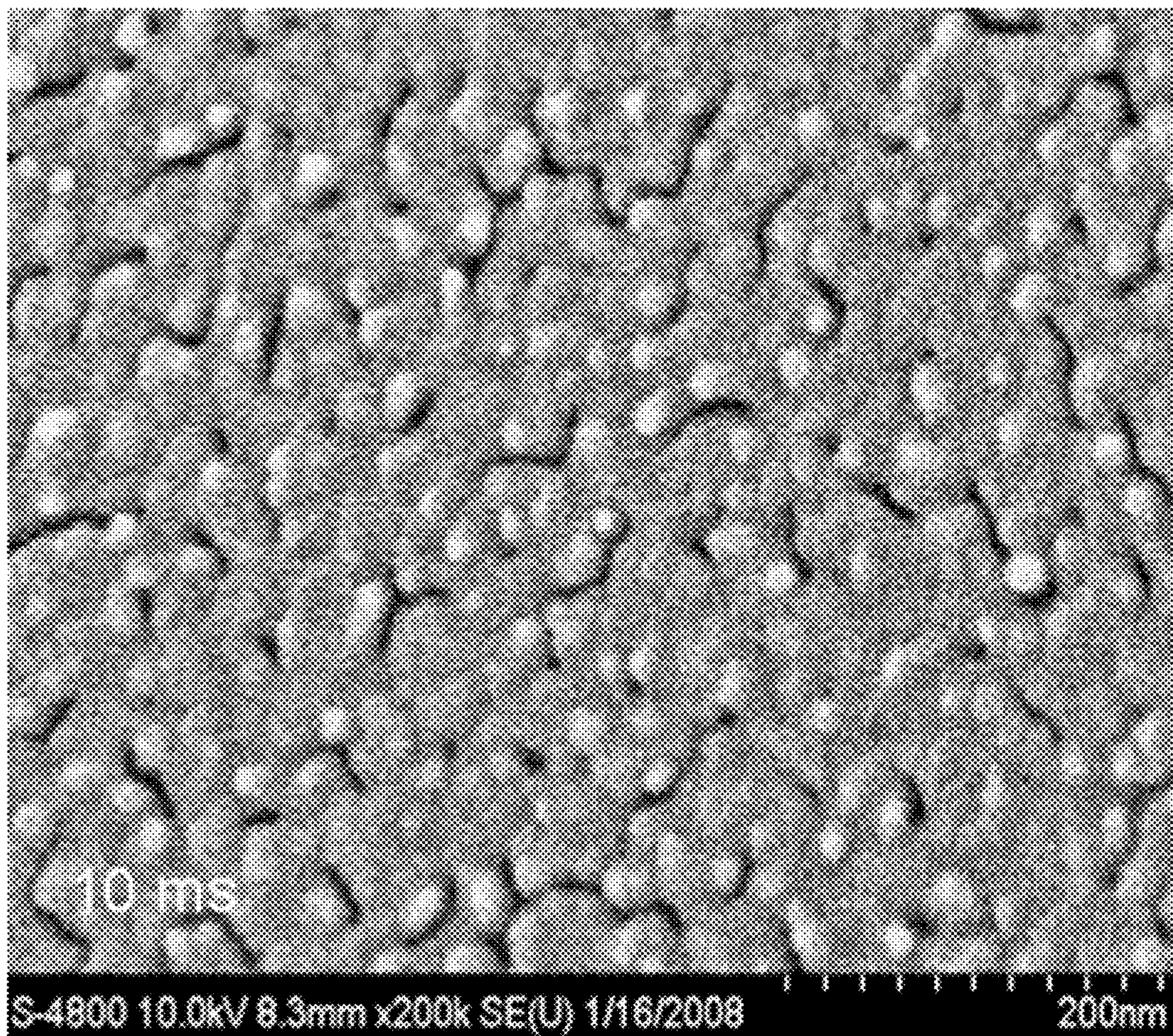
50ms



20ms

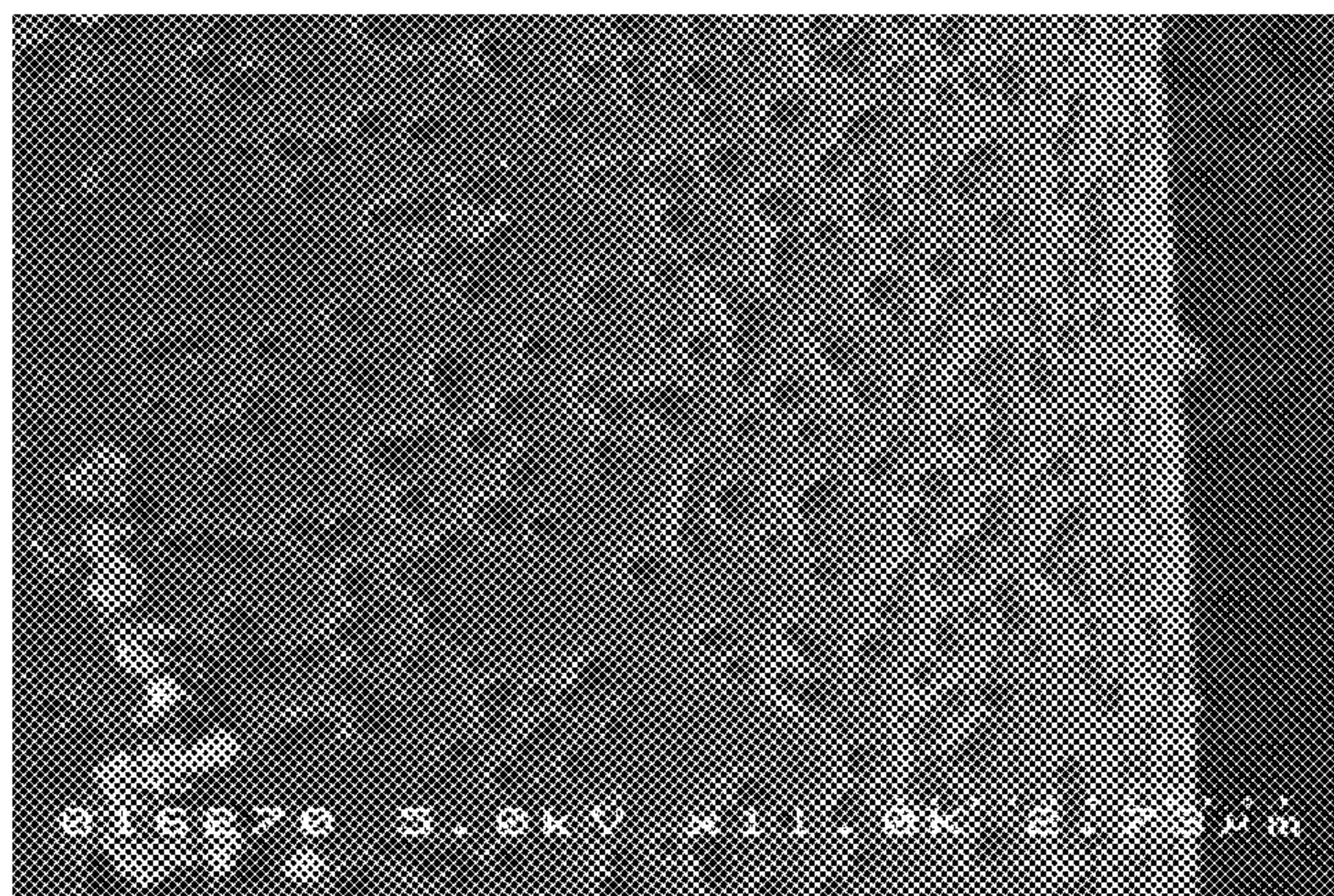
FIG. 3

10 cycles of 10 ms - Even coverage with nanoparticles less than 20 nm

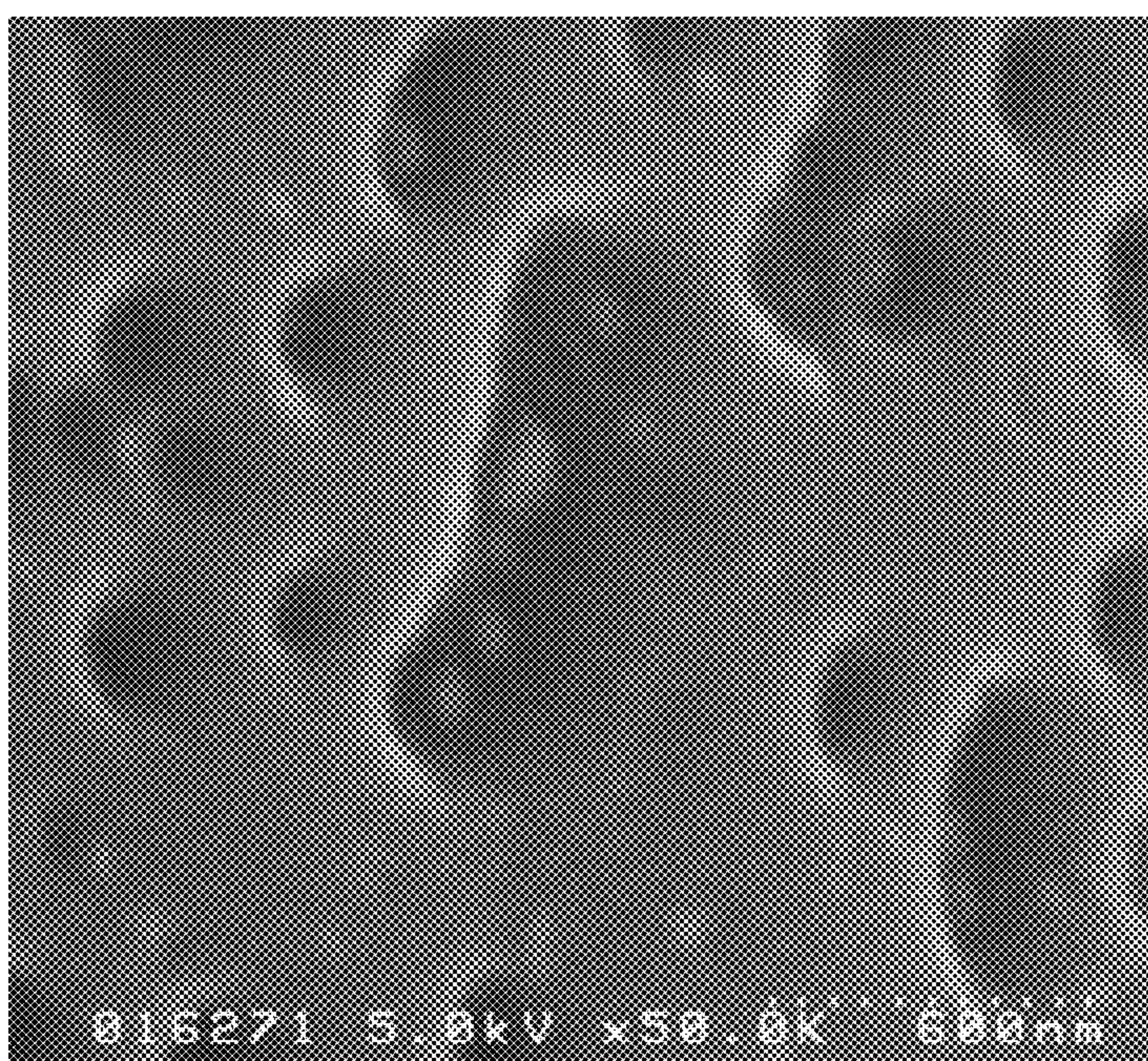


Electrodeposited Ni, 1.18 V_{SCE}, 0.4 molar H₃BO₃ plus 0.3 molar NiSO₄

FIG. 4

Nanoparticle Size and Pit Formation

Kynol carbon fiber
0.25 wgt.% Ni(acac)₂ in THF
(3x) activated in 1:1 air:N₂ @
800°C for 7 minutes



Kynol carbon fiber
0.25 wgt.% Ni(acac)₂ in
THF (3x) activated in 1:1
air:N₂ @ 800°C for 7
minutes

(magnified view)

FIG. 5

Effect of High Nanoparticle Coverage on Pore Formation

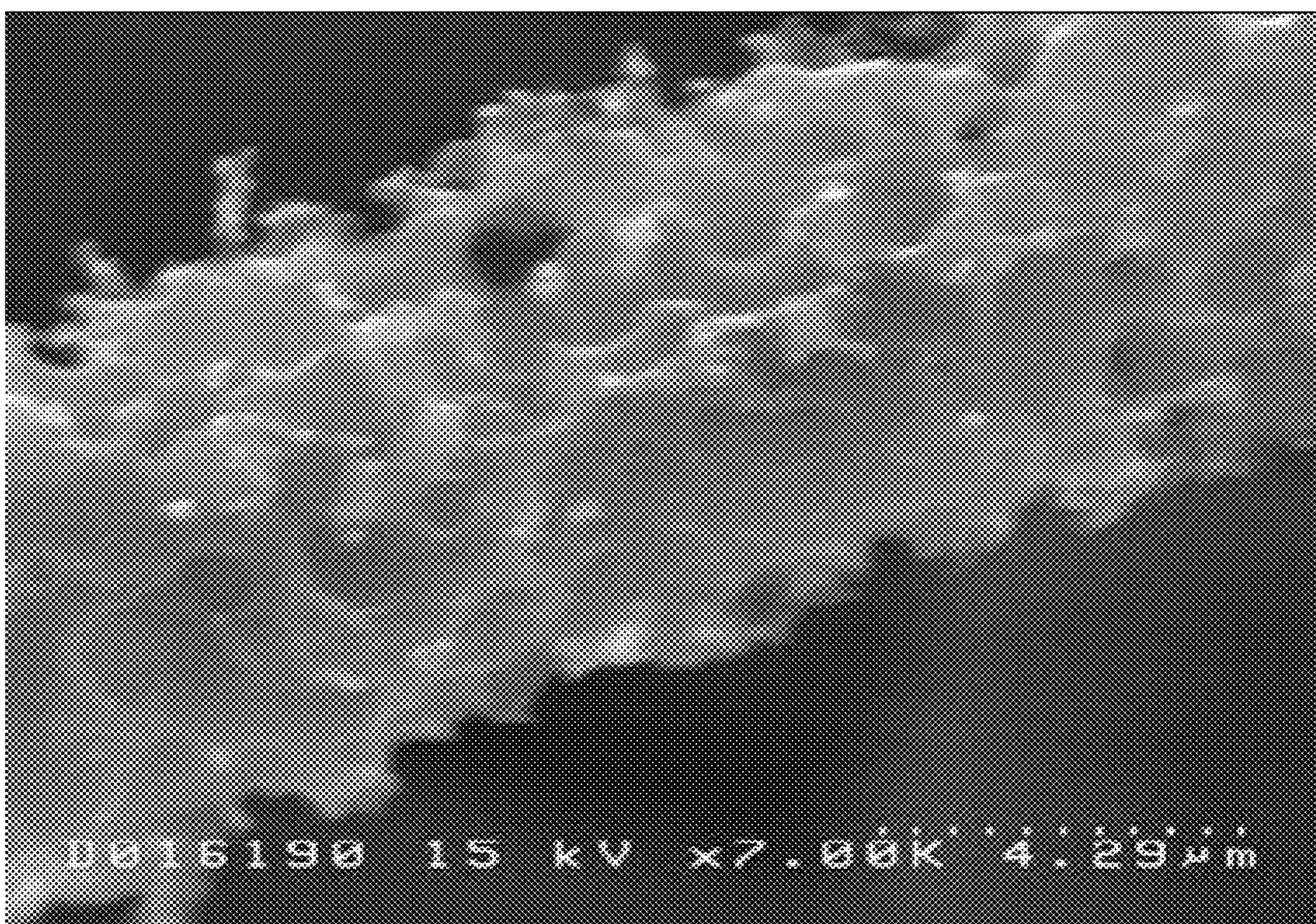


FIG. 6

CONTROLLED ELECTRODEPOSITION OF NANOPARTICLES

TECHNICAL FIELD

[0001] The present invention relates to activated carbons and to methods for their preparation. The activated carbons may be used in all manner of devices that may contain activated carbon materials, including but not limited to various electrochemical devices (e.g., capacitors, batteries, fuel cells, and the like), hydrogen storage devices, filtration devices, catalytic substrates, and the like.

BACKGROUND OF THE INVENTION

[0002] In many emerging technologies, such as electric vehicles and hybrids thereof, there exists a need for capacitors with both high energy and high power densities. Much research has been devoted to this area, but for many practical applications such as hybrid electric vehicles, fuel cell powered vehicles, and electricity microgrids, the current technology is marginal or unacceptable in performance and too high in cost. See *DOE Progress Report for Energy Storage Research and Development fy2005 (January 2006)* and *Utility Scale Electricity Storage by Gyuk, manager of the Energy Storage Research Program, DOE (speaker 4, slides 13-15, Advanced Capacitors World Summit 2006)*.

[0003] Electrochemical double layer capacitors (EDLC's, a form of electrochemical capacitor called an ultracapacitor, sometimes also called a supercapacitor) are one type of capacitor technology that has been studied for such applications. Electrochemical double layer capacitor designs rely on very large electrode surface areas, which are usually made from "nanoscale rough" metal oxides or activated carbons coated on a current collector made of a good conductor such as aluminum or copper foil, to store charge by the physical separation of ions from a conducting electrolyte into a region known as the Helmholtz layer that forms immediately adjacent to the electrode surface. See U.S. Pat. No. 3,288,641. There is no distinct physical dielectric in an EDLC. Nonetheless, capacitance is still based on physical charge separation across an electric field. The electrodes on each side of the cell and separated by a porous membrane store identical but opposite ionic charges at their surfaces within the double layer, with the electrolyte solution in effect becoming the opposite plate of a conventional capacitor for both electrodes.

[0004] It is generally accepted that EDLC internal carbon pore size should be at least about 2 nm for an aqueous electrolyte or at least about 3 nm for an organic electrolyte to accommodate the solvation spheres of the respective electrolyte ions in order for the pores to contribute their surface for Helmholtz double layer capacitance. See *J. Electrochem. Soc.* 148(8): A910-A914 (2001) and *Electrochem. and Solid State Letters* 8(7): A357-A360 (2005). Internal pores also should be accessible from the outer particle surface for electrolyte exposure and wetting, rather than sieving. The more total accessible surface, the better. Conventional activated carbons used in ELDC devices have many electrochemically useless micropores (i.e. below 2 nm according to the IUPAC definition). In the highly activated electrochemical carbons reported in the literature, utilized surface is typically thought to be 10% (see U.S. Pat. No. 6,491,789) to 20% (see U.S. Pat. No. 6,737,445). A typical mesopore proportion in commercial electrocarbons may range from a low of 5% to a high of 22% mesopore with DFT surfaces ranging from about 1300

m²/g to about 1900 m²/g. See *Walmet (MeadWestvaco), Proceedings of the 16th International Seminar on DLC (ISDLC): 139-140 (2006)*.

[0005] Several alternative approaches to producing a high usable surface carbon suitable for EDLC devices using organic electrolytes at their desirable higher operating voltages have been undertaken. These include unusual carbon precursors (for example, U.S. Pat. No. 6,660,583), novel carbonization regimes (for example U.S. Pub. No. 2005/0207961), novel physical activation regimes lasting many hours or even days (for example those mentioned by Norit Nederland BV—a major activated carbon supplier—in *Proceedings of 16th ISDLC: 95 (2006) as "steam activation at 800-1000C" with residence time in the kiln "from several hours to several days"*), novel chemical activation regimes (for example, U.S. Pat. No. 5,877,935), carbon aerogels (for example, U.S. Pat. No. 5,626,977, U.S. Pat. No. 5,898,564), various templating techniques (for example U.S. Pat. No. 6,297,293, U.S. Pub. No. 2004/0091415, U.S. Pat. No. 6,737,445), carbide derived carbons (for example, PCT/EE2005/000007, U.S. Pub. No. 2006/0165584) and carbon nanotubes (for example, U.S. Pat. No. 6,491,789 and U.S. Pat. No. 6,934,144) or equivalents (for example, U.S. Pub. No. 2005/0025974). Each of these approaches has significant limitations.

[0006] An application by one of these inventors, PCT/US2007/004182 (claiming priority to U.S. Provisional Application No. 60/773,538, filed Feb. 15, 2006), analyzes these limitations, and discloses a novel method of producing improved mesoporous carbons from any suitable precursor by use of catalytic nanoparticles. A further application by one of these inventors, U.S. patent application Ser. No. 12/070,062, filed Feb. 14, 2008, discloses additional novel methods for forming and utilizing catalytic nanoparticles for improved mesoporous carbons.

[0007] For applications including electrochemical capacitors, hybrid capacitor/battery devices such as Fuji Heavy industries LiC, and asymmetric batteries it is desirable to precisely engineer the mesoporous carbon to the requirements of the device (energy density, power density, electrolyte system) by suitably adjusting the induced mesoporosity

BRIEF SUMMARY OF THE INVENTION

[0008] The scope of the present invention is defined solely by the appended claims, and is not affected to any degree by the statements within this summary.

[0009] In order to address these issues, there is a need for improved control of nanoparticle catalyzed mesopore formation in carbons.

[0010] In one embodiment, there is a method for forming metallic nanoparticles on the surface of a carbon. Metal and/or metal oxide ions are deposited on a carbon surface by electrodeposition. One electrodeposition process includes applying a number of electrical pulses having a pulse width. The number of electrical pulses may be between 5 and 50, and the pulse width may be between 5 milliseconds and 200 milliseconds. In another embodiment, the carbon is anodized before electrodeposition. If the carbon is a carbon precursor, after electrodeposition, the carbon precursor is carbonized to form a carbon.

[0011] In another embodiment, there is a method for forming metallic nanoparticles on the surface of a carbon. Electrodeposition is utilized to deposit metal ions on carbon surface. The number of nanoparticles per unit carbon exterior

surface area may be affected by controlling the number of electrical pulses used for deposition. The average diameter of nanoparticles placed onto the carbon exterior surface may be affected by controlling the duration of electrical pulses used for deposition. The composition of nanoparticles placed on the surface of the carbon particles may be affected by controlling the chemical composition of the conductive precursor chemical solution. Alloy nanoparticles can be made, combining attributes of different elements such as catalytic rate or pseudocapacitive potential.

[0012] In a method for forming an activated carbon, metal ions are electrodeposited on a surface of a carbon, to form metallic nanoparticles on the surface of the carbon. The carbon is then activated.

[0013] In yet another embodiment, there is a method of preparing a mesoporous carbon with enhanced rugosity and proximate exterior. Metal ions are electrodeposited on a surface of the carbon to form nanoparticles on the surface of the carbon. If the carbon is a carbon precursor, the precursor is carbonized to form a carbon. The carbon may be activated by catalytically activating the carbon in air and an inert gas to form a catalytically activated carbon, where the mass of the catalytically activated carbon is lower than the mass of the carbon. The catalytically activated carbon may be physically activated in steam or carbon dioxide to form an activated carbon; where the mass of the activated carbon is lower than the mass of the catalytically activated carbon. During activation, the nanoparticles preferentially etch mesoporous ‘tunnels’ into the surface of the carbon particles, thereby enhancing carbon surface rugosity. The resulting activated carbon is mesoporous.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 contains photographs showing metallic/metal oxide nanoparticles and carbon surfaces formed by coating organometallic precursors with solvents of varying concentrations, followed by thermal decomposition.

[0015] FIG. 2 contains photographs showing metallic/metal oxide nanoparticles and carbon surfaces formed by electrodeposition with a varying number of voltage cycles.

[0016] FIG. 3 contains photographs showing metallic/metal oxide nanoparticles and carbon surfaces formed by electrodeposition with a varying pulse width.

[0017] FIG. 4 contains photographs showing metallic/metal oxide nanoparticles and carbon surfaces formed by electrodeposition with a preferred number of pulse cycles and a preferred pulse width.

[0018] FIG. 5 contains photographs showing metallic/metal oxide nanoparticles and carbon surfaces formed by coating organometallic precursors with solvents of varying concentrations, followed by partial thermal decomposition.

[0019] FIG. 6 contains a photograph illustrating the potential effects of high nanoparticle coverage on mesopore formation.

DETAILED DESCRIPTION OF THE INVENTION

[0020] Enhanced methods of engineered nanoparticle deposition on carbon and conductive carbon precursors have been discovered and are described herein. General nanoparticle catalytic activation means enhancing the rugosity and proximate exterior of carbon materials have been described in U.S. patent application Ser. No. 11/211,894, filed Aug. 5, 2005, and U.S. patent application Ser. No. 12/070,062, filed

Feb. 14, 2008, the entire contents of each are incorporated herein by reference, except that in the event of any inconsistent disclosure or definition from the present application, the disclosure or definition herein shall be deemed to prevail. Throughout this description and in the appended claims, the following definitions are to be understood:

DEFINITIONS

[0021] The term “rugosity” used in reference to carbons refers to the difference between actual surface area and theoretical geometric area in accordance with the definition in the IUPAC Compendium of Chemical Terminology, 2nd edition (1997). For example, the sand side of a sheet of ordinary sandpaper has substantially higher rugosity than the paper side.

[0022] The term “particle” used in reference to precursors and activated carbons refers to a distribution of materials conventionally from about 1 micron to more than 100 microns in diameter. Such particles can be conventionally prepared prior to and/or after physical or chemical activation, as described, for example, in U.S. Pat. No. 5,877,935, U.S. Pat. No. 6,643,119 and U.S. Pat. No. 7,214,646.

[0023] The phrase “fiber” used in reference to polymers and carbons refers to filamentous material of fine diameter, such as diameters less than about 20 microns, and preferably less than about 10 microns. Such fibers can be obtained using conventional solvent or melt spinning processes or by unconventional spinning processes such as electrospinning. Such fibers, when fragmented into short pieces (as with conventional ‘milled’ carbon fiber at about 150 microns length with aspect ratios of 15 to 30 from fiber diameters conventionally at least 7 microns), as used herein also comprise ‘particles’.

[0024] The term “mesoporous” as used in reference to a carbon describes a distribution of pore sizes wherein at least about 20% of the total pore volume has a size from about 2 nm to about 50 nm in accordance with the standard IUPAC definition.

[0025] The phrase “catalytically activated” as used in reference to a carbon refers to its porous surface wherein mesopores have been formed from the external surface of the carbon particle or fiber toward the interior by a catalytically controlled differential activation (e.g., etching) process. In some embodiments, metal and/or metal oxide particles of a chosen average size serve as suitable catalysts and a least a portion of the metal oxides remain in or on the carbon after the activation process.

[0026] The phrase “nanoparticle” as used in reference to catalytic particles means a nanoscale material with an average particle diameter greater than 2 nm and less than 100 nm.

[0027] There are a variety of design considerations when manufacturing an activated carbon. The precursor carbon may come from any source of sufficient purity to be used as an electrocarbon (either with or without an additional final chemical purification step such as acid washing), including naturally occurring materials such as coals, plant matter (wood, coconut shell, food processing remainders (pulp, pith, bagasse), or sugars), various petroleum or coal tar pitches, specialized pitch precursors such as described by U.S. Pat. No. 6,660,583, or from synthetic polymeric materials such as polyacrylonitrile (PAN) or polyvinylidene chloride (PVDC). The present invention is not limited thereto but comprises any chemically suitable precursor capable of being carbonized, and activated.

[0028] In some embodiments, a metal-containing material, such as a metal oxide nanoparticle or a precursor thereto, is introduced during one or more of the processing stages to provide catalytic surface sites for the subsequent etching of surface pores during the activating stage and/or to provide a desired electrochemical activity. The metal or metals of the metal containing materials are selected based on their catalytic and/or electrochemical activities.

[0029] In some embodiments, the nanoparticles have diameters of up to and including about 50 nm, in other embodiments, up to and including about 15 nm, in other embodiments, up to and including about 8 nm, in other embodiments, up to and including about 4 nm, and in other embodiments, about 2 nm. The preferred particle size mode will depend on the choice of electrolyte and the device requirements. For example power density may preferably have larger surface mesopores to reduce diffusion and migration hindrance and local depletion, at the expense of less total surface and lower energy density.

[0030] It is generally accepted that EDLC pore size should be at least about 1-2 nm for an aqueous electrolyte or about 2-3 nm for an organic electrolyte to accommodate the solvation spheres of the respective electrolyte ions in order for the pores to contribute surface available for Helmholtz layer capacitance. Pores also should be open to the surface for electrolyte exposure and wetting, rather than closed and internal. At the same time, the more total open pores there are just above this threshold size the better, as this maximally increases total surface area. Substantially larger pores are undesirable because they comparatively decrease total available surface. Research by others has shown that capacitance improves as average pore size increases from about 4 to about 28 nm, and that optimum pore size with organic electrolytes ranged from about 15 to about 25 nm.

[0031] In some embodiments, the metal and/or metal oxide nanoparticles comprise iron, nickel, cobalt, titanium, ruthenium, osmium, rhodium, iridium, yttrium, palladium, or platinum, or combinations thereof, or alloys thereof. In some embodiments, the metal/oxide nanoparticles comprise nickel oxide. In some embodiments, the metal/oxide nanoparticles comprise iron oxide. In some embodiments, the nanoparticles comprise alloys of nickel and iron.

[0032] Carbon mesoporosity and total surface resulting from catalytic nanoparticle activation is a function of metal or metal oxide type (catalytic potency), nanoparticle size, nanoparticle loading (i.e. the coverage on the carbon, the number of nanoparticles per unit carbon exterior surface), carbon precursor, and carbon activation conditions such as temperature, etchant gas (i.e. steam or carbon dioxide or air) content as a percentage of the neutral (e.g. nitrogen) atmosphere, and duration of activation.

[0033] A metal-containing material may be introduced using an organometallic metal oxide precursor or a mixture of such precursors. In one embodiment, the metal oxide precursor preferably comprises a metal acetylacetonate, such as a nickel acetylacetonate. In another example, the metal oxide precursor comprises metal acetate with an alcohol as a solvent, such as nickel acetate.

[0034] When metallic/metal oxide nanoparticles are formed by such general solvent coating methods using organometallic precursors followed by thermal decomposition into nanoparticles, the resulting nanoparticles can have substantially varying average sizes, and the nanoparticle coverage density can vary on different carbons. Two experimental

carbons illustrate this difference. The first carbon is unactivated but fully carbonized Kynol fiber precursor (available from American Kynol, Inc., Pleasantville, N.Y.) averaging about 13 microns in diameter. The second carbon is an anthracite coal "Minus 100" particulate powder averaging about 4.7 microns in diameter, with high purity and good conductivity. Nanoparticles of both iron and nickel were formed by solvent deposition of 0.1% (metal:carbon weight) metal acetylacetonate dissolved in tetrahydrofuran (THF), followed by evaporation of the solvent and then catalytic nanoparticle formation by thermal decomposition under nitrogen, and resulting mesopore formation using a 1:1 ratio of air:nitrogen at 800° C. for either 7 or 10 minutes.

[0035] Nanoparticles of nickel or iron ranging from 40 nm to 60 nm on the Kynol fiber were visible near the limit of resolution of the SEM (scanning electron microscope) instrument. No nanoparticles were visible at the SEM limit of resolution on the anthracite coal "Minus 100" particulate powder. The large, widely spaced nanoparticles formed on the Kynol fiber are attributable to a paucity of nucleation sites. Carbonized Kynol has 'annealed pores' that are relatively impervious even to activation gasses, and thus presents comparatively few places for nanoparticles to preferentially precipitate during thermal decomposition.

[0036] Consequently, increasing the metal acetylacetonate concentration tends to increase nanoparticle size more than coverage. This is demonstrated by varying the concentration of $\text{Ni}(\text{acac})_2$ from 0.1% to 0.25% to 0.5% to 1.0% on Kynol, and imaging the resulting nanoparticles and carbon surfaces. FIG. 1 contains photographs showing metallic/metal oxide nanoparticles and carbon surfaces formed by coating organometallic precursors with solvents of varying concentrations, followed by thermal decomposition. Two experiments were performed to illustrate the effect of metal acetylacetonate concentration on the formation of nanoparticles. In one experiment, carbonized Kynol fiber was sprayed three times with 0.25% concentration $\text{Ni}(\text{acac})_2$ in THF, then activated in 1:1 air: N_2 at 800° C. for 7 minutes. In a second experiment, carbonized Kynol fiber was sprayed twice with 1.0% concentration $\text{Ni}(\text{acac})_2$ in THF, then calcined in air at 350° C. for 7 minutes. The images show the difference in nanoparticle formation as a function of the concentration of $\text{Ni}(\text{acac})_2$.

[0037] While some of the post-processing steps differ in the experiments, the effect of metal acetylacetonate concentration is apparent by comparison of the images. At 1.0% concentration of $\text{Ni}(\text{acac})_2$, nanoparticles tend to range from about 80 nm to over 150 nm in diameter, while at 0.25% nanoparticles tend to range from about 40 nm to about 70 nm. At 1.0%, the nanoparticle coverage was only about twice as dense as at 0.25%.

[0038] As stated above, no nanoparticles were visible at the SEM limit of resolution on the anthracite coal "Minus 100" particulate powder. The small nanoparticles on the "Minus 100" are attributable to its abundant nucleation sites. This difference in nucleation sites is demonstrated by comparing the surface results, measured using the Brunauer, Emmett and Teller (BET) method, of uncoated materials that are simply steam activated for 60 minutes at 900° C. The Kynol fiber produced a BET surface of 112 square meters, while the anthracite coal "Minus 100" particulate powder produced a BET surface of 801 square meters. The catalytic presence of small nanoparticles (not imaged with the SEM instrument) is demonstrated by equivalent steam activation after coating: a BET surface of 965 square meters of surface was achieved

with 0.1% iron acetylacetonate coating compared to a BET surface of 801 square meters without.

[0039] Natural precursor materials such as coal present a further challenge because of the variation in the number of nucleation sites per unit area from sample to sample of the same precursor material. The variation of nucleation sites may cause coverage variations in the nanoparticles formed by coating organometallic precursors with solvents. Thus, mesopore formation, and hence capacitance, may vary across activated carbons formed from different samples of the same type of precursor material.

[0040] Thus it is useful to have improved control of nanoparticle formation for catalytic activation of mesoporous carbons.

[0041] It is known in the art that metals can be deposited on conducting surfaces electrochemically, using electrical field potential to cause metal ions in a conducting solvent bath (such as water with salts added) to migrate to a counter-charged surface and deposit thereon. This is the basic principle behind electroplating. See *Modern Electroplating 3rd edition*, (Frederick A. Lowenheim ed., John Wiley & Sons 1974). It is also known in the art that pre-existing particles of conducting materials can be migrated and attached to a conducting surface under electric field potential. Any colloidal particle capable of forming a stable suspension in a liquid and which can carry an electric charge may be migrated through an electric field (electrophoresis) and deposited on an electrode material. Such particles include pigments, polymers, dyes, ceramics (i.e. metal oxides), and metals. This general class of well-known industrial processes is called electrophoretic deposition, and is widely used, for example in electrophoretic painting of automobiles. However, the process requires the prefabrication of the colloidal particles for the suspension.

[0042] It has surprisingly been discovered that with appropriate electrical control, metallic and/or metal oxide nanoparticles may be formed directly from a chemical bath and deposited onto carbon or conducting carbon precursors with control of size, coverage, and composition. The general control mechanisms for this nanoparticle electrodeposition process are number of electrical pulses for nanoparticle coverage (more pulses produce more particles per unit surface area), and relative pulse width (i.e. pulse duration) for particle size (shorter pulses produce smaller particles). Solution chemistry determines the nanoparticle composition.

[0043] The general process setup for the illustrative examples is as follows. A suitable aqueous chemical precursor bath is prepared. In one embodiment, for formation of nickel nanoparticles, the bath may comprise 0.4 molar H_3BO_3 plus 0.3 molar NiSO_4 held at a temperature of 65° C. to 70° C. and magnetically stirred. Carbon (such as Kynol fibers) serves as the deposition cathode, and the anode is a graphite disk. Electrical pulses are generated by a standard potentiostat, such as the EG&G Princeton Applied Research Model 273A.

[0044] The carbon (such as Kynol fibers) may also be pre-processed before electrodeposition using a chemical anodization process. Anodization may aid to functionalize the surface of the carbon, and thus, may enhance the uniform nucleation of the metal nanoparticles on the surface of the carbon fiber. In one embodiment, anodization is performed at a constant potential, 0.850 V_{SCE} for 10 minutes, in a chemical bath containing about 18.65% H_2SO_4 . Other chemical bath chem-

istries for anodization are possible, and known in the art. Kynol fibers are the deposition cathode, and the anode is a graphite disk.

[0045] By way of illustration of the utility of this invention, nickel nanoparticles were deposited using the methods herein to varying degrees of coverage and nanoparticle size depending on the number of electrical pulses for nanoparticle coverage, and the relative pulse width (i.e. pulse duration) for particle. The same principles apply to deposition of iron nanoparticles, although the results are not presented here.

[0046] In one set of experiments, nickel is electrodeposited on carbon utilizing a magnetically stirred nickel electrochemical bath of 0.4 molar H_3BO_3 plus 0.3 molar NiSO_4 held at a temperature of 65° C. to 70° C., and a 1.18 V_{SCE} , 1 Hz, 50% duty cycle (e.g. pulse 'on' duration was equal to pulse 'off' duration) input, for a varying number of cycles. Kynol fibers are the deposition cathode, and the anode is a graphite disk. FIG. 2 contains photographs showing metallic/metal oxide nanoparticles and carbon surfaces formed by electrodeposition with a varying number of voltage cycles. In the experiments, the number of pulse cycles was varied from 10 (low coverage) to 60 (high coverage). Each pulse was substantially greater than 100 milliseconds (with equal pause times between pulses), so that the resulting large nanoparticles are easily imaged by a SEM at about 10 k magnification. As is readily apparent from the comparative images for nickel in FIG. 2, a preferred number of pulse cycles is less than 30, and at least about 10. Further, the experiments illustrate that for electrodeposition utilizing different configurations, including other metals, nanoparticle coverage may be adjusted by varying the number of pulse cycles.

[0047] In another set of experiments, nickel is electrodeposited on Kynol fiber utilizing a magnetically stirred nickel electrochemical bath of 0.4 molar H_3BO_3 plus 0.3 molar NiSO_4 held at a temperature of 65° C. to 70° C., and a 10 cycles of a 1.18 V_{SCE} input, with varying pulse width (pulse duration). Kynol fibers are the deposition cathode, and the anode is a graphite disk. Before electrodeposition, anodization of the Kynol fiber was performed at a constant potential, 0.850 V_{SCE} for 10 minutes, in a chemical bath containing 18.65% H_2SO_4 . FIG. 3 contains photographs showing metallic/metal oxide nanoparticles and carbon surfaces formed by electrodeposition with a varying pulse width. In the experiments, the effect of pulse width is determined by holding the number of cycles constant and varying the pulse width (pulse duration) from 20 milliseconds to 500 milliseconds, with the 'off' pause between pulses held constant at 1 second. A decrease in average nanoparticle size with decreasing pulse width (duration) is readily apparent from the comparative images of FIG. 3, which show the resulting nanoparticles and carbon surfaces as viewed using a FEM (field emission microscope) at 200 k magnification. As shown in FIG. 3, 20 millisecond pulses produce nanoparticles substantially below 20 nm in diameter. Further, the experiments illustrate that for electrodeposition utilizing different configurations, including other metals, nanoparticle diameter may be adjusted by varying the pulse width (duration).

[0048] In one embodiment, the sets of experimental results may be utilized to deposit nanoparticles on carbon with a preferred nanoparticle coverage and preferred nanoparticle size, by selecting a number of electrical pulses for nanoparticle coverage, and by selecting a pulse width, respectively. FIG. 4 contains photographs showing metallic/metal oxide nanoparticles and carbon surfaces formed by electrodeposi-

tion with a preferred number of pulse cycles and a preferred pulse width. In this embodiment, a $1.18 V_{SCE}$ input having a pulse width of 10 milliseconds is utilized, with 10 pulses per electrodeposition cycle. Kynol fibers are the deposition cathode, and the anode is a graphite disk. A magnetically stirred nickel electrochemical bath of 0.4 molar H_3BO_3 plus 0.3 molar $NiSO_4$ is used, held at a temperature of $65^\circ C.$ to $70^\circ C.$ The deposition process takes just over 10 seconds. As shown in FIG. 4, the resulting nanoparticles are uniformly substantially smaller than 20 nm, with many less than 10 nm, as directly imaged using a FEM (field emission microscope) at 200 k magnification. As compared to the example utilizing 10 cycles of pulse input shown in FIG. 2, the coverage is similarly dense and reasonably uniform. Further, the electrodeposition results shown in FIG. 4 tend to be more easily reproducible than nanoparticles formed using general solvent coating methods using organometallic precursors followed by thermal decomposition. The reproducibility of electrodeposition results may facilitate mass production of activated carbons, and hence other products such as capacitors, having substantially similar area and electrical properties, respectively.

[0049] While not shown in FIG. 4 and the accompanying text, chemical anodization may be utilized before the electrodeposition process in order to improve the uniformity of the distribution of the nanoparticles formed on the surface of the carbon. Functionalizing the surface of the carbon through anodization may enhance the uniformity of nucleation sites on the carbon fiber, thereby facilitating a more uniform distribution of nanoparticles formed on the carbon fiber during electrodeposition. Thus, in another embodiment, a carbon fiber may be anodized utilizing a constant potential, $0.850 V_{SCE}$ input for 10 minutes, in a chemical bath containing 18.65% H_2SO_4 . Nickel ions may be electrodeposited on the resulting anodized carbon using a $1.18 V_{SCE}$ input having a pulse width of 10 milliseconds, with 10 pulses per electrodeposition cycle. Anodized Kynol fibers are the deposition cathode, and the anode is a graphite disk. A magnetically stirred nickel electrochemical bath of 0.4 molar H_3BO_3 plus 0.3 molar $NiSO_4$ may be utilized, held at a temperature of $65^\circ C.$ to $70^\circ C.$ After electrodeposition, improved uniformity of the distribution of the formed nanoparticles was observed.

[0050] After an electrodeposition process is completed, activation (e.g., treatment with steam in a relatively inert atmosphere of N_2 at or above about $750^\circ C.$, treatment with carbon monoxide, treatment with carbon dioxide, treatment with air containing oxygen, or any combination of such treatments) may create a preponderance of open fiber surface mesopores substantially all above 2 nm, and preferably above 5 nm, such as are desirable for EDLCs. Ultimate pore density (and total surface porosity) with average pore size above the size of the catalyst nanoparticle is a function of metal oxide type (catalytic potency), nanoparticle size, particle loading, and carbon activation conditions such as temperature, pressure, and duration. Nickel oxide is inexpensive compared to cobalt or ruthenium, and may desirably be used as a pseudocapacitive pore catalyst that has been shown to be less reactive during carbon activation than either iron or cobalt. Further, nickel oxide may be capable of more nanoparticle loading for higher total surface activation, and for more pseudocapacitance. It has been shown by others that the oxide nanoparticles will largely remain exposed in the carbon fiber pores they create, and therefore, will be available to contribute pseudocapacitance with aqueous electrolytes.

[0051] Further, the embodiment illustrates that for electrodeposition utilizing different configurations, including other metals, a preferred nanoparticle diameter and a preferred nanoparticle coverage may be simultaneously achieved by selecting the pulse width and the number of pulse cycles, respectively. Nanoparticle diameter and nanoparticle coverage are dependent parameters that may be selected to maximize the capacitance of the resulting activated carbon. As previously discussed, research by others has shown that capacitance improves as average mesopore size increases from about 4 nm to about 28 nm, and that optimum mesopore size with organic electrolytes ranged from about 15 nm to about 25 nm. The coverage, or density, of nanoparticles formed is dependent on the desired nanoparticle diameter. For example, if nanoparticle coverage is zero percent, then no catalytic etching will occur. On the other hand, if nanoparticle coverage is one hundred percent, then no mesopores will be formed, because the entire carbon surface area will be etched away.

[0052] FIG. 5 illustrates the effect of nanoparticle diameter and nanoparticle coverage on mesopore formation. FIG. 5 contains photographs showing metallic/metal oxide nanoparticles and carbon surfaces formed by coating organometallic precursors with solvents of varying concentrations, followed by partial thermal decomposition. Nanoparticles of nickel were formed by solvent deposition of 0.1% (metal:carbon weight) metal acetylacetonate dissolved in tetrahydrofuran (THF), followed by evaporation of the solvent and then catalytic nanoparticle formation by thermal decomposition under nitrogen, and resulting mesopore formation using a 1:1 ratio of air:nitrogen at $800^\circ C.$ for 7 minutes. As evident from the photographs, for this exemplary metal oxide type (catalytic potency), nanoparticle size, and carbon activation conditions such as temperature, pressure, and duration, pore diameter is approximately three times the diameter of the nanoparticle.

[0053] Further, the local variation in nanoparticle coverage caused by the coating process is useful for illustrating the effect of coverage on pore formation. Referring to the Kynol fiber in FIG. 5, some local regions contain no nanoparticles, and thus, the Kynol fiber does not contain etched pores. On the other hand, under magnification, it is evident that nanoparticles spaced too closely to one another are no longer separated by Kynol fiber sidewalls, because the sidewalls separating the nanoparticles have been etched away, creating a single large pore in a region containing several adjacent nanoparticles (a local area of high nanoparticle coverage).

[0054] FIG. 6 contains a photograph illustrating the potential effects of high nanoparticle coverage on mesopore formation. Other reactive conditions may also contribute to mass loss, such as an activation temperature higher than preferred, an activation duration longer than preferred, or a concentration of reactive gas that is higher than preferred.

[0055] However, a high coverage of nanoparticles can also contribute to mass loss. If nanoparticle coverage is too high, optimal pore structures will not be formed, because the sidewalls between pores formed by adjacent nanoparticles will be partially or completely etched away. When catalytic etching results in loss of substantially all of the surface of a carbon, the creation of pores favorable for the capacitive properties of an EDLC is reduced.

[0056] Thus, for a given mesopore diameter, a preferred nanoparticle density allows the formation of separate, adjacent pores, separated by sidewalls of carbon of a minimum strength to avoid collapse of the sidewalls. The diameter of a

mesopore is a function of the chemical composition of the nanoparticles and the activation conditions, such as the carbon material, temperature, and other reactive conditions.

[0057] In one embodiment, a preferred nanoparticle diameter and preferred nanoparticle coverage may maximize the capacitance (measured in F/g) of the resulting activated carbon, or increase the capacitance of the activated carbon beyond a required (but achievable) threshold. Hence, the pulse width and the number of pulse cycles that may achieve a preferred nanoparticle diameter and preferred nanoparticle coverage may be experimentally determined by forming activated carbons with activation and most electrodeposition parameters constant, and iterating through combinations of electrodeposition pulse width and pulse cycles. For each experimental combination of pulse width and number of pulse cycles, the measured capacitance of the resulting activated carbon is measured and compared with the previous experimental results, until one or more combinations that achieve a maximum, local maximum, or minimum required (but achievable) capacitance is identified.

[0058] One skilled in the art will realize that by varying the chemical composition of the precursor bath, nanoparticles of varied composition (for example, alloys of iron/nickel) may be made with coverage density and size control as herein generally described.

[0059] In another embodiment, the Kynol fibers may be preprocessed before electrodeposition using a chemical anodization process. Anodization may aid to functionalize the surface of the carbon, and thus, may enhance the uniform nucleation of the metal nanoparticles on the surface of the carbon fiber. The foregoing electrodeposition process experiments described in FIGS. 2-4 and the accompanying text may optionally utilize carbon fibers preprocessed with an anodization step before electrodeposition. By doing so, the uniformity of nanoparticle distribution on the surface of the carbon fiber may be improved. A more uniform nanoparticle distribution may facilitate the formation of separate, adjacent pores, separated by sidewalls of carbon of a minimum strength to avoid collapse of the sidewalls.

[0060] This invention discloses a novel means of further controlling nanoparticle size, coverage density, and composition, usefully providing surprisingly precise control over carbon mesoporosity produced by catalytic activation. Electrodeposition of nanoparticles avoids the coverage variation of nanoparticles formed by coating organometallic precursors with solvents. The coverage variation is at least partially avoided because electrodeposition depends to a lesser degree on nucleation sites for nanoparticle formation, where the number of nucleation sites per unit area may vary from sample to sample of natural precursor materials and some synthetic precursor materials. Hence, electrodeposition can achieve more easily repeatable nanoparticle formation results across multiple samples of the same type of precursor material. Anodization before electrodeposition may aid to functionalize the surface of the carbon, and thus, may be utilized to enhance the uniform nucleation of the metal nanoparticles on the surface of the carbon fiber.

[0061] After electrodeposition, the carbon may be activated. The nanoparticles may serve as catalysts for activation rugosity of mesoporous carbons. The catalytically activated carbon materials may be used in all manner of devices that contain carbon materials, including various electrochemical

devices (e.g., capacitors, batteries, fuel cells, and the like), hydrogen storage devices, filtration devices, catalytic substrates, and the like.

[0062] The foregoing detailed description has been provided by way of explanation and illustration, and is not intended to limit the scope of the appended claims. Many variations in the presently preferred embodiments illustrated herein will be apparent to one of ordinary skill in the art, and remain within the scope of the appended claims and their equivalents.

1. A method of forming metallic nanoparticles on the surface of a carbon, comprising:

electrodepositing metal ions on the surface of the carbon, the electrodepositing comprising:

applying a plurality of electrical pulses, each electrical pulse having a pulse width, wherein the number of electrical pulses is between 5 and 50, and the pulse width is between 5 milliseconds and 200 milliseconds.

2. The method of claim 1, wherein the carbon is a carbon precursor.

3. The method of claim 2, wherein the carbon precursor is conductive.

4. The method of claim 1, wherein electrodepositing metal ions further comprises immersing the carbon and an anode in a salt bath having a chemistry, wherein the metallic nanoparticle composition is determined by the chemistry of the salt bath.

5. The method of claim 1, wherein the nanoparticles comprise at least one of: nickel or iron.

6. The method of claim 1, wherein the nanoparticles are less than D_{50} 50 nm.

7. The method of claim 1, wherein the pulse duration is less than 50 milliseconds.

8. The method of claim 1, wherein the number of electrical pulses is less than 30.

9. The method of claim 1, further comprising anodizing the carbon before electrodepositing metal ions.

10. A method comprising:

electrodepositing metal ions on a surface of a carbon, to form metallic nanoparticles on the surface of the carbon; and

activating the carbon to form an activated carbon.

11. The method of claim 10, wherein the carbon is a carbon precursor.

12. The method of claim 11, wherein the carbon precursor is conductive.

13. The method of claim 11, further comprising carbonizing the precursor to form a carbon.

14. The method of claim 10, wherein electrodepositing metal ions further comprises immersing the carbon and an anode in a salt bath having a chemistry, wherein the metallic nanoparticle composition is determined by the chemistry of the salt bath.

15. The method of claim 10, wherein the nanoparticles comprise at least one of: nickel or iron.

16. The method of claim 10, wherein the nanoparticles are less than D_{50} 50 nm.

17. The method of claim 10, wherein the pulse duration is less than 50 milliseconds.

18. The method of claim 10, wherein the number of electrical pulses is less than 30.

19. A method of forming an activated carbon:

(a) providing a carbon which is either a carbon or a carbon precursor;

- (b) electrodepositing metal ions on the surface of the carbon to form nanoparticles on the surface of the carbon;
- (b2) if the carbon is a carbon precursor, then carbonizing the precursor to form a carbon; and
- (c) activating the carbon to form an activated carbon.

20. The method of claim **19**, wherein activating the carbon comprises:

catalytically activating the carbon in air and an inert gas to form a catalytically activated carbon; wherein the mass of the catalytically activated carbon is lower than the mass of the carbon; and

physically activating the catalytically activated carbon in steam or carbon dioxide to form an activated carbon; wherein the mass of the activated carbon is lower than the mass of the catalytically activated carbon and wherein the activated carbon is mesoporous.

21. The method of claim **19** wherein the nanoparticles comprise at least two different metal oxides.

22. The method of claim **19** wherein the nanoparticles comprise at least one of: iron, nickel, cobalt, titanium, ruthenium, osmium, rhodium, iridium, yttrium, palladium, or platinum.

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