



- (51) **International Patent Classification:**
B22F 1/00 (2006.01) *B22F 9/24* (2006.01)
- (21) **International Application Number:**
PCT/GB2015/051264
- (22) **International Filing Date:**
30 April 2015 (30.04.2015)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
1407755.6 2 May 2014 (02.05.2014) GB
- (71) **Applicant:** UNIVERSITY OF WARWICK [GB/GB];
University House, Kirby Corner Road, Ellough, Coventry
West Midlands CV4 8UW (GB).
- (72) **Inventors:** SADLER, Peter; University of Warwick, Uni-
versity House, Kirby Corner Road, Coventry, West Mid-
lands CV4 8UW (GB). BARRY, Nicolas; University of
Warwick, University House, Kirby Corner Road, Coventry,
West Midlands CV4 8UW (GB). BEANLAND, Richard;

University of Warwick, University House, Kirby Corner
Road, Coventry, West Midlands CV4 8UW (GB). **PITTO-
BARRY, Anais;** University of Warwick, University
House, Kirby Corner Road, Coventry, West Midlands CV4
8UW (GB).

- (74) **Agents:** HGF LIMITED et al.; Document Handling -
HGF (Birmingham), Belgrave Hall, Belgrave Street, Bel-
grave Street, Leeds, Yorkshire LS2 8DD (GB).
- (81) **Designated States** (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States** (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,

[Continued on next page]

(54) Title: NANOCRYSTALS

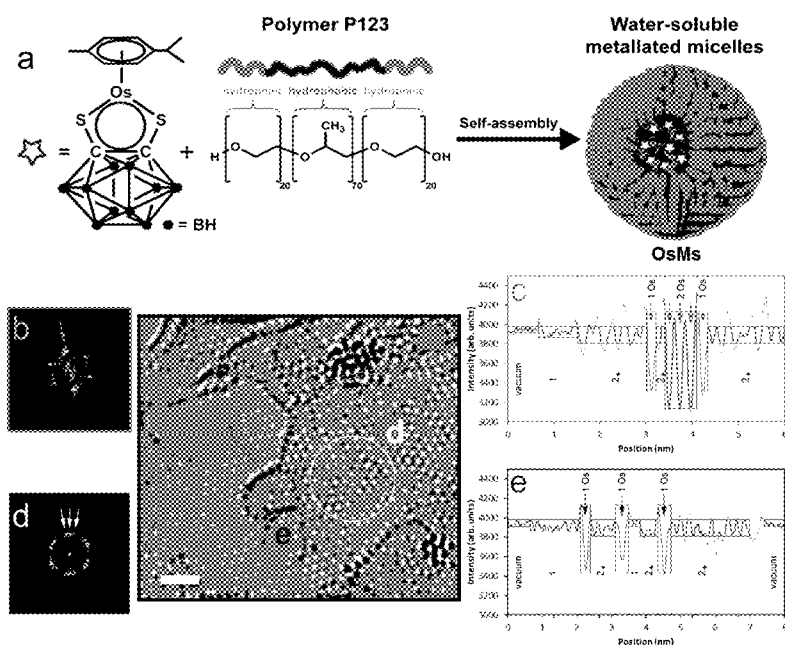


Figure 1

[Continued on next page]



GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT,
LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE,

SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(57) Abstract: A method of producing single metal atoms on a graphitic surface, the method comprising the steps of: • providing a metal complex; • mixing the metal complex with a carbon-containing species to form an encapsulant comprising the metal complex encapsulated by the carbon-containing species; • depositing the encapsulant; and • irradiating the deposited encapsulant to form a graphitic surface on which one or more isolated metal atoms of the metal complex are located.

Nanocrystals

This invention relates to nanocrystals and methods of fabricating the same. The invention also relates to methods of producing graphene (and/or graphene-like substances) and describes surfaces which may be used to study atomic processes.

Introduction

Tailoring nanoscopic objects is of importance for the production of the materials of the future, for example in medicine, industrial manufacturing, construction, and space exploration¹⁻⁴. The potential for use of metal nanocrystals has long been recognized. For example, colloidal gold was first made by Andreas Cassius in 1685⁵, and notably also by Michael Faraday in 1857⁶. Since then, a range of techniques has allowed the fabrication of nanocrystals, and these have allowed detailed investigation of their size-dependent properties⁷. The recent emergence of powerful methods such as high-resolution transmission electron microscopy, has allowed the design and the observation of a variety of nanometer-sized objects, from graphene matrices, to nanoparticles and nanotubes^{8,9}.

The process of crystallization, the formation of microscopic periodic arrangements of atoms, ions and molecules, has long been a topic of intense fascination. It is 100 years since William Henry Bragg and his son William Lawrence Bragg revolutionized the characterization of crystalline solids by showing that the atomic structure of a crystal is related to its x-ray diffraction pattern¹⁰. Understanding the dynamics of crystal formation is also of great interest since the mode of assembly can influence the type of periodic lattice which is formed, and hence the properties of the resulting crystals. However, the direct observation of resolved single atoms, atom-by-atom cluster formation, and the crystallization process for nanoscopic crystals is still an experimental frontier.¹¹⁻¹⁵ Currently, formation of such crystals cannot be controlled at the level of individual atoms¹⁶⁻²⁰, and understanding the metal dynamics of nanocrystal formation relies mostly on computation¹⁸⁻²⁰.

Objects of the invention

It is one object of this invention, and here we introduce, a new general method for the fabrication of graphitic matrices, preferably doped graphitic matrices and most preferably multi-heteroatom-doped graphitic matrices, some, one or all of which may be decorated with metal

crystals, preferably 3D-metal crystals and most preferably very small, Ångstrom-sized, 3D-metal crystals of defined size. This invention facilitates experimental observation of crystal assembly from single metal atoms and is able to capture the dynamics of metal cluster formation in real space with atomic precision. In one embodiment we irradiate boron-rich precious-metal complexes encapsulated in self-spreading polymer micelles with electrons and produce, in real time, a doped graphitic support on which individual metal atoms hop and migrate to form 3D-nanocrystals, as small as 15 Å in diameter and within 1 hour. Crystal growth can be observed, quantified and controlled in real time. An aspect of the invention is exemplified by osmium, the densest of all metals²¹, and is capable of giving rise to osmium crystals which are amongst the smallest reported²², for example embedded into a B/S-doped graphitic support. As an example of the generality of the procedure, and in another embodiment we have also synthesized the first examples of mixed ruthenium-osmium 3D-nanocrystals. The invention, at least in one or more aspects not only allows the production of Ångstrom-sized homo- and hetero-crystals, highly novel materials with potentially useful and unusual properties, but also provides new experimental insight into the dynamics of nanocrystals and pathways for their assembly from single atoms.

Accordingly, a first aspect of the invention provides a method of producing single metal atoms on a surface, the method comprising the steps of:

- a. providing a metal complex;
- b. mixing the metal complex with a carbon-containing species to form a mixture;
- c. depositing the mixture; and
- d. irradiating the deposited mixture to form a graphitic surface on which one or more of the metal atoms are located.

A further aspect of the invention provides a method of producing single metal atoms on a graphitic surface, the method comprising the steps of:

- a. providing a metal complex;
- b. mixing the metal complex with a carbon-containing species to form an encapsulant comprising the metal complex encapsulated by the carbon-containing species;
- c. depositing the encapsulant; and
- d. irradiating the deposited encapsulant to form a graphitic surface on which one or more isolated metal atoms of the metal complex are located.

In this specification, 'encapsulated' includes at least partially encapsulated. The encapsulant may comprise a micelle, reverse micelle, vesicle, lipid bilayer, nanocapsules, nanoparticles, metal organic frameworks (MOF), and is most preferably a micelle.

5

Further, in this specification 'isolated' in the context of the metal atoms means that the metal atoms are no longer complexed, or at least are associated with fewer ligands or complexing agents than prior to irradiation.

10 The ligands of the metal complex may comprise carbon. Irradiation may cause the carbon containing ligands and/or the carbon containing species to form the graphitic surface.

In the method step d may be conducted by heating, for example by irradiating with infrared energy, or step d may be conducted by irradiating with high energy radiation, typically greater
15 than 1 pA cm^{-2} . The irradiating step d may be conducted in both oxidizing and non-oxidising atmospheres (for example *in vacuo* or in air).

Preferably the mixture is irradiated, preferably with high energy radiation, for sufficient time to allow or cause plural metal atoms to agglomerate on the surface. Most preferably the deposited
20 mixture is irradiated for sufficient time to allow or cause plural metal atoms to agglomerate on the surface to form clusters, and preferably for sufficient time to allow or cause metal atoms to agglomerate to form nanoalloys and/or nanocrystals. The method may be continued to grow larger alloys and/or crystals.

25 In one embodiment the deposited mixture is irradiated for up to 1hr thereby to produce nanocrystals typically of 0.5 to $60 \times 10^{-9} \text{ m}$, and preferably from $1.5 - 50 \times 10^{-9} \text{ m}$ in diameter. It has been found that the degree of irradiation (dose, time) can be selected to generate nanocrystals of specific size. This opens a convenient and attractive route for the generation of specific size nanocrystals.

30

Plural metal complexes each based on a different metal and mixing at least one of the complexes in the, or each in a respective, carbon-containing species may be provided.

Advantageously, it has been surprisingly discovered that by selecting a particular molar ratio of the plural metals in the plural metal complexes it is possible to generate an alloy (for example a nanoalloy) and/or a mixed metal nanocrystal with a mixing ratio substantially the same as the molar ratio. This opens a very attractive route for easily producing nanoalloys and/or heteroatomic nanocrystals of a specific mixing ratio.

Step a may comprise providing a metal complex in which the metal is selected from molybdenum, tungsten, tin, lead, arsenic, antimony, and bismuth, indium, gallium, osmium, ruthenium, rhodium, platinum, palladium, iridium, gold, silver, cobalt, iron, nickel, chromium, manganese, vanadium, lanthanides, e.g. Ru^{II} or Os^{II}, and the ligands may be selected from an arene or cyclopentadienyl derivative, together with, for example, one or more, for example at least 2 other ligands, e.g. a dithio-carborane.

Conveniently, wherein step b may comprise mixing the metal complex with a polymer, typically in a solvent or a mixture of solvents, for example tetrahydrofuran/water (e.g. 1:10 v/v). The polymer may be a di or tri-block copolymer. Preferably said mixing causes the polymer to form one or more of vesicles, lipid bilayer, micelles, nanocapsules, nanoparticles, metal organic frameworks (MOF), thereby to encapsulate the metal complex.

The method may also comprise providing as at least a component of a ligand of the metal complex, a species able to dope the graphitic structure upon irradiation, for example upon exposure to the heat energy, preferably high energy radiation. This conveniently allows *in situ* production of doped graphitic, graphene or graphene-like, substances. The dopants can be selected as part of the ligand. Clearly the amount to which the so-formed graphene is doped will likely depend, at least in part, on the amount of dopant in the complex

Step d may be conveniently practiced by use of one or more of an electron beam, a laser beam, UV light, plasma, microwaves, γ -rays, heat gun (*i.e.* infrared irradiation), although conductive heating may also be deployed. We prefer a laser beam or an electron beam.

If an electron beam is used it is possible to change the voltage of the electron beam to control nanoparticle fabrication times and the size of the crystals. Altering the intensity and/or energy of the irradiation allows varying irradiation times to be used for producing crystals under conditions

which preserve the underlying graphitic matrix, thus allowing longer irradiation times and the fabrication of larger crystals of, typically, 20 nm to 50 nm in diameter

A further aspect of the invention provides a method of forming metal nanocrystals, the method comprising exposing a metal complex suspended in a carbon-containing matrix to heat energy, preferably high energy radiation, allowing or causing metal atoms to agglomerate to form nanocrystals and harvesting the nanocrystals.

A yet further aspect of the invention provides a method of forming metal nanocrystals, the method comprising exposing a metal complex encapsulated in a fluid, carbon-containing matrix to heat energy, preferably high energy radiation, to form a graphitic substrate and allowing or causing metal atoms to agglomerate on the graphitic substrate to form nanocrystals and harvesting the nanocrystals.

The harvesting may comprise dissolving or otherwise removing a substrate on which the nanocrystals are located. In one embodiment the substrate is graphene, or graphene-like, which may be conveniently formed from the carbon matrix and removing the substrate comprises dissolving the graphene.

The method may comprise forming a micelle containing the complex, thereby suspending the complex in the carbon-containing matrix.

Another aspect of the invention provides a method of agglomerating metal atoms, the method comprising providing plural individual metal atoms on a graphitic surface, preferably comprised of one or more layers of graphene, and irradiating the surface to allow or cause the metal atoms to agglomerate.

The irradiation may be continued for sufficient time to allow or cause atoms to agglomerate to form nanoalloys or nanocrystals.

The irradiation may be provided by a beam of high energy radiation, for example an electron beam, laser beam, focused UV light or IR radiation. This conveniently allows a known portion of the surface to be irradiated, thereby allowing or causing metal agglomeration in a particular desired location.

A further aspect of the invention provides a solvent-soluble micelle comprising a polymeric shell containing a substantially solvent-insoluble metal complex, the or at least one of the ligands comprising one or more of boron, phosphorus, nitrogen, sulfur, selenium, tellurium and the metal being selected from molybdenum, tungsten, tin, lead, arsenic, antimony, and bismuth, indium, gallium, osmium, ruthenium, rhodium, platinum, palladium, iridium, gold, silver, cobalt, iron, nickel, chromium, manganese, vanadium, lanthanides.

In one embodiment the metal of the metal complex may be indium, gallium, ruthenium and/or osmium, e.g. Ru^{II} or Os^{II}, and the ligands preferably comprise an arene or cyclopentadienyl derivative, together with one or more, for example at least 2 other ligands, e.g. a dithio-carborane.

In one embodiment at least one of the ligands may comprises a chalcogen (for example one or more of sulphur, selenium, tellurium, oxygen) or a halogen (for example one of iodine, bromine) or a pnictogen (for example one of nitrogen, phosphorous, arsenic, antimony). The ligand may comprise a dithio-carborane or diselenate-carborane. In certain embodiments wherein, upon irradiation in step d said chalcogen, halogen or pnictogen preferably dopes the graphitic structure.

The micelle may further comprise a second solvent insoluble metal complex, wherein the second metal is different from the first. The second metal may be selected from molybdenum, tungsten, tin, lead, arsenic, antimony, and bismuth, osmium, ruthenium, rhodium, platinum, palladium, iridium, gold, silver, cobalt, iron, nickel, chromium, manganese, vanadium, lanthanides.

Preferably the micelle is formed from di-block or tri-block copolymers. A suitable tri-block polymer is P123. The micelles of this polymer self-assemble and forms stable films. This is convenient when seeking to study the so-formed graphitic structures.

A yet further aspect of the invention provides a method of forming graphene, the method comprising irradiating micelles, lipids, vesicles or other carbon-containing species with high energy radiation. We prefer to use an electron beam for our experiments but other high energy

radiation sources may be used such as a laser beam, UV light, plasma, heat gun, microwaves, x-rays, and γ-rays.

Advantageously, at least some of the micelles may contain and or encapsulate a species able to
5 dope the graphene surface. Such dopants may be selected from boron, phosphorus, nitrogen, sulfur, selenium, tellurium. This is advantageous because it provides a route for producing doped graphitic surfaces (for example for providing hot spots for nanocrystal growth). The dopant may form at least a part of a ligand. Alternatively or additionally, the micelles may comprise (*e.g.* may encapsulate) a metal. The metal may form part of a complex, for example a
10 complex with the dopant forming at least a part of one or more ligands. The metal may catalyse graphene formation and/or dopant uptake.

A fourth aspect of the invention provides a self-supporting graphitic structure comprising one or more dopants and one or more individual metal atoms movably located on the surface of the
15 structure.

The dopant may be selected from boron, phosphorus, nitrogen, sulfur, selenium, tellurium. The metal may be selected from one or more of molybdenum, tungsten, tin, lead, arsenic, antimony, and bismuth, osmium, ruthenium, rhodium, platinum, palladium, iridium, gold, silver, cobalt, iron,
20 nickel, chromium, manganese, vanadium, lanthanides. Preferably the graphitic structure comprises at least one other, different metal, which may be selected from the above list.

The graphitic structure provides a convenient substrate on which to examine the movement and/or clustering behaviours of metals. Indeed, and as we show below, it is possible to monitor
25 in real-time the movements of what appears to be individual atoms.

A further aspect of the invention provides a three dimensional nanocrystal comprising ruthenium and osmium.

30 In order that the invention may be more fully understood, it will now be described, by way of example only, and with reference to the accompanying drawings, in which:

Figure 1 Micelle formation and analysis after irradiation with electrons.

Self-assembly of block copolymer micelles **OsMs** containing encapsulated osmium carborane complex (**b-e**): A typical area after degradation of the micelles by irradiation showing formation of a self-supporting graphitic matrix and individual osmium atoms (scale bar: 1 nm), characterized as follows: (**b**) Fast Fourier transform corresponding to single-sheet graphene-like material at the edges of the material, blue circle. (**c**) Intensity plot along the green line; the difference in thickness of the graphitic matrix (single layer vs 2 or more layers) is evident from the range of intensities (pink bands), similarly the difference between single and stacked Os atoms is evident for the cluster of atoms (green arrows), demonstrating its 3D nature. (**d**) Fast Fourier transform corresponding to a three-layer graphene-like material, yellow circle. (**e**) Detection of single Os atoms along the red line.

Figure 2 Electron energy loss elemental mapping of nanoclusters and self-supported graphitic matrix. (a) Sulfur L, (b) boron K, and (c) osmium O maps. (d) Osmium and sulfur superimposed maps. (e) Osmium and boron superimposed maps. (f) Osmium, sulfur, and boron superimposed maps. On each map, the element(s) appear(s) as bright spots when present. For instance, osmium atoms are localized in regions of crystals, and appear to be close to high-boron and high-sulfur sites, although boron and sulfur atoms are also observable throughout the lattice. All the images show the same region.

Figure 3 Time-dependent formation of Os nanocrystals on the graphitic matrix. (**a-d**) Migration of small clusters and their coalescence (e.g. clusters in yellow and dark blue circles merge to give crystal in green circle) over a period 1-30 min; scale bars: 2 nm. (**e**) The abundance of nanocrystals after 60 min. (**f**) Typical example of an Os crystal of ca. 1.5 nm, formed after 30 min of irradiation, scale bar: 1.5 nm. (**g**) Width of the clusters/crystals *versus* time. The error bars represent the disparity of width of the clusters, measured on each picture. (**h**) Fast Fourier transform analysis of the nanocrystal shown in f.

Figure 4. Migration and fusion of energized osmium clusters leading to the growth of nanocrystals. Images recorded after electron beam irradiation times of (**a**) 10 min, (**b**) 20 min, (**c**) 25 min, and (**d**) 30 min, showing the fusion of two clusters (yellow and blue balls for Os atoms of each cluster) into a larger fused cluster (green balls).

Figure 5. Montage of 10 Os nanocrystals with their FFT analysis.

Figure 6. Experimental and simulated crystal structure comparisons. (**a.** and **b**) Two nanocrystals with close resemblance to hexagonal structure. (**c.** and **d**) Simulations along the c-axis and a-axis, respectively.

Figure 7. Ru-Os 3D-nanocrystals from RuOsMs micelles. (**a**) An array of mixed metal nanocrystals on the graphitic support formed after 60 min of irradiation (scale bar: 10 nm), with enlargement of the blue circled crystal showing atomic resolution (scale bar: 2 nm) and Fast Fourier transform analysis of the hexagonal mixed metal crystal. The Fast Fourier transform analysis of the hexagonal mixed metal crystal is also shown in the enlargement. (**b**) 3D projection (left) of the same crystal showing the difference of contrast between Ru, Os and the background (each peak corresponds to an atom, and the height/intensity of the peaks is dependent on the atomic TEM contrast; arbitrary colors), also depicted as 29 red (Os) and 28 green (Ru) balls on the 2D projection (right). The presence of Ru and Os atoms was confirmed by a combination of STEM and EDX analysis.

Figure 8. Combination of scanning-TEM (STEM) and energy-dispersive X-ray (EDX) analysis. (**a.** and **b**) Two areas are shown; the bright spots correspond to nanocrystals. The table shows the EDX analysis for four crystals, along with the Ru/Os molar ratio.

Figure 9. Pattern of single Os atom 'hopping'. (**a**) A hexagonal graphene lattice and the three possible atomic positions (edge = red; bridge = green; hole = blue). Each type has a distinct set of vectors between equivalent sites, indicated by arrows. (**b**) Each dot represents the observed jump size for one single Os atom in a time frame of 200 seconds (each point represents one jump, and 20 jumps were considered); Horizontal lines correspond to the theoretical jump size (*i.e.* vector lengths in **a**) for edge-to-edge (red lines), bridge-to-bridge (green lines), and hole-to-

hole (blue lines) patterns of hopping. (c) Changes of position and (d) jump direction for this single Os atom in the same time frame of 200 s (20 frames, with 10 seconds between each frame).

Figure 10. **HR-TEM image of a cluster of 3 Os atoms, and 3D projection.** In the projection, the Os atoms can be seen because of their higher contrast as compared to the graphitic matrix (yellow-red peaks).

Figure 11. **Two views of a dinuclear Os_2 molecule on the distorted graphitic matrix.** The two Os atoms are in light blue.

Figure 12. **Atom-by-atom formation of osmium molecules clusters and eventually crystals.** (a) 3D projection showing high contrast for a single Os atom, together with three 2D projections showing movement of the Os atom at a rate of 0.0177 nm/s over a period of 160 s. (b-c) Formation of dimer, trimer and tetramer molecules. (d) A cluster of eight Os atoms. (e) A 15 Å crystal. All the images show the same region. In further images (f) and (g) Formation of larger nanoparticles after 24h irradiation of the **OsMs** micelles with the electron beam of a transmission electron microscope operating at 200 keV (scale bars: 20 nm (f), 10 nm (g)).

Figure 13. **UV-visible spectra:** P123Ms (10^{-4} M in H_2O ; blue line), complex 1 (10^{-3} M in CH_3CN ; red line), and **OsMs** (10^{-4} M in H_2O ; black line). The change of color from transparent P123Ms to purple **OsMs** shows that 1 is encapsulated in the polymer micelles.

Figure 14. **Characterization of polymer micelles by dynamic light scattering (DLS).** (a) Size distribution in number of P123Ms and **OsMs** (10 mg/mL in H_2O); Intensity, volume and number distribution for (b) P123Ms, and (c) **OsMs**; 10 mg/mL, H_2O . These experiments show that polymer P123 and complex 1 self-assemble in aqueous solution.

Figure 15. **Characterization of polymer micelles by cryogenic-TEM (cryo-TEM).** (a) Cryo-TEM image of **OsMs**. (b) Particle counting/histogram analysis of **OsMs** from cryo-TEM images.

Figure 16. **Characterization of polymer micelles by small-angle x-ray scattering (SAXS).** (a) Small-angle X-ray scattering (SAXS) experimental profiles and fitting with the PolyCoreShellRatio model of micelles **OsMs** and (b) P123Ms; 1 mg/mL aqueous solutions.

Figure 17. **Small-angle X-ray scattering (SAXS) profiles.** (a) **OsMs** and (b) P123Ms, at three different concentrations (1; 5; 10 mg/mL) showing small structure-factor effects at higher concentrations but the micellar structure which does not change significantly with concentration for both P123Ms and **OsMs**.

Figure 18. **Dry-state TEM images of the self-assembled polymer **OsMs** micelles on Quantifoil® grids (scale bar: 1 μm),** demonstrating that **OsMs** spread and form stable nanostructures in the dry-state (with a diameter ca. 30 fold larger in the dry-state than for spherical micelles in solution).

Figure 19. **Positions, trajectory, and experimental hopping of an Os atom on the B/S- and B/Se-doped graphenic surfaces.** (a) 3D-projection of HRTEM images showing the position of an Os atom on the B/S surface at different irradiation times (time = 0 s corresponds to the first image of the stack), and HRTEM image of an Os atom on the surface (Os spot is arrowed). (b) Three examples of trajectories for the hopping of an individual Os atom on the B/S surface over 390 s, and (c) on the B/Se surface over 15 s. (d) Cumulative apparent distances covered by an individual Os atom on B/S (yellow) and B/Se (blue) surfaces. (e) Apparent speed of motion of an individual Os atom on B/S (yellow) and B/Se (blue) surfaces between each frame (t being set at 0 for the first frame of each stack). (f) Enlargement of the B/S (yellow) plot shown in (e).

Figure 20. **Positions, trajectory, and experimental hopping of Os_2 molecules on the B/S- and B/Se-doped graphenic surfaces.** (a) HRTEM images showing the position of the two Os atoms on the B/S surface at different irradiation times (time = 0 s corresponding to the first image of the stack; scale bar = 0.5 nm). 3D surface projection of each TEM picture, showing the topography of the surface beneath the Os atoms. (b) Trajectory of the hopping of the two Os atoms on the B/S surface over 390 s. (c) Trajectory of the hopping of the two Os atoms on the B/Se surface over 15 s. (d) Distances covered by each Os atom of a diatomic molecule on B/S

(black and red) and B/Se (light and deep blue) surfaces. (e) Jump size against time for each atom of the molecule on the B/Se surface.

Figure 21. **Analysis of the mechanism of hopping of individual Os atoms on the two graphenic surfaces.** (a) and (b) Histograms of pooled jumps of individual Os atoms on B/S and B/Se surfaces, respectively. (c) and (d) Normal Quantile-Quantile plot of Os atoms hopping on B/S and B/Se surfaces, respectively.

Figure 22. (a) Self-assembly of block copolymer metallated micelles containing encapsulated metal (Os, Ru, Ir, or Au) carborane complex. (b) Cartoon of the methodology used in this work: 1. Electron beam irradiation of the metallated micelles; 2. Degradation and production of a graphenic surface on which individual metal atoms can hop and migrate; 3. Metal nucleation and formation of small molecules made of metals, and clusters; 4. Eventual metal nanocrystal formation.

Figure 23. Examples of Ru, Os, Ir, and Au nanocrystals with corresponding fast Fourier transform (left) and respective crystal growth *versus* irradiation time (right). Scale bar 1 nm.

Figure 24. Shows various stages in the formation of gold nanocrystals and nucleation steps (from 5 to 40 minutes of irradiation).

Figure 25 Provides a sequential series of TEM images at different magnification showing the irradiation of micelles on a silicon nitride surface.

Figure 26 Provides a series of TEM images showing the formation of nanocrystals through irradiating by a laser beam, and

Figure 27 shows a series of TEM images showing the formation of nanocrystals through irradiation by microwaves.

Results:

Preparation of precursors

Our procedure involved the encapsulation of the organometallic half-sandwich Os^{II} arene complex [Os(*p*-cymene)(1,2-dicarba-*c*/oso-dodecarborane-1,2-dithiolate)] (**1**) (a 16-electron complex²³ which is highly hydrophobic²⁴) in the water-soluble amphiphilic triblock copolymer P123²⁵ at ambient temperature for 4 h to form **OsMs** micelles (Fig. 1). The **OsMs** micelles were fully characterized by a range of techniques, including synchrotron small-angle x-ray scattering experiments (see Methods below). These analyses demonstrated that complex **1** and polymer P123 self-assemble in solution to give core/shell micelles with very low dispersity parameters (0.161), containing 52±6 P123 unimers, along with 52±11 complex **1**. They have a core-diameter of 9.06±0.12 nm, and a shell-diameter of 6.50±0.15 nm, giving a total-diameter of 15.56±0.27 nm. The data are summarized in Table 1.

Table 1. Physical characteristics of OsMs and P123Ms micelles determined by DLS, cryo-TEM and SAXS at 1 mg/mL.

Micelles	OsMs	P123Ms
----------	------	--------

Polymer aggregation number	52±6	20±2
Os complexes per micelle	52±11	0
DLS diameter (nm)	11.50±2.35	19.60±1.80
DLS dispersity	0.030	Not determined
Cryo-TEM diameter (nm)	7.85±1.97	Not determined
Cryo-TEM dispersity	1.06	Not determined
SAXS total diameter (nm)	15.56±0.27	18.96±0.23
SAXS core diameter (nm)	9.06±0.12	6.74±0.06
SAXS shell diameter (nm)	6.50±0.15	12.22±0.17
SAXS dispersity	0.161	0.146

OsMs micelles are dispersed in water, they contain a defined number of metal complexes, and are deformable on surfaces. P123 polymer forms stable Langmuir films at ambient temperature²⁶. Thus, we deposited aqueous droplets ([**OsMs**] = 1 mg/mL) onto lacey carbon-coated grids to produce an unsupported film over the grid holes for examination by aberration-corrected high resolution transmission electron microscopy (HR-TEM).

Formation of a graphitic matrix and Os nanocrystals

We observed structural changes within the Pluronic[®] film upon irradiation with the high-energy electron beam (80 keV; 1.9 pA·cm⁻² or 7.6×10⁷ electrons·nm⁻²·s⁻¹). The emergence of atomic ordering within the self-supporting matrix consistent with a turbostratic graphitic structure was apparent within a few minutes, and a highly-structured few-layer graphene (FLG) lattice was evident after 50 min. An analysis of this matrix is shown in Figure 1. The existence of individual layers of single-sheet graphene-like material at the edges of the material was demonstrated by fast Fourier transform (FFT) analysis (Figure. 1b), whilst few-layer graphene-like material was also visible (Figure. 1c shows a region with three layers). Along with these structural modifications of the self-supporting polymeric film, a rapid decomposition of the carborane-containing complex **1** was also observed (in less than one minute), and Os atoms could be imaged either singly or as small ordered clusters (Figures. 1c, 1e), which is currently at the forefront of such experiments^{9,17,27,28}.

Electron energy loss spectroscopy (EELS) not only confirmed the identity of the Os atoms, but also suggested that boron and sulfur from the carborane ligand in **1** are present in the graphitic matrix (See Figure 2). Notably, sites with Os clusters (Supplementary Fig. 2c) appear to be

close to both high-boron (Supplementary Figures 2b, 2e, 2f), and high-sulfur sites (Supplementary Figures 2a, 2d, 2f). Interestingly, boron and sulfur atoms are also seen throughout the entire matrix suggesting the formation of a multi-heteroatom-doped graphitic matrix. After 1 min of irradiation, clusters of ca. 0.7 nm were already visible (Figure 3a). After 5 min of irradiation, dark areas containing ca. 15 atoms, became more organized and larger (ca. 1.0 nm, Figure 3b). Further growth of the nanoclusters on the self-supporting matrix was evident after 15 min of irradiation (Figure 3c), and after 30 min, osmium metal clusters with diameters of ca. 1.2 to 1.6 nm were visible (Figure 3d). Growth was observed until ca. 60 min (Figures 3e and 3f), and the nanoclusters were seen to roll on the support in a series of images recorded within a minute. The movement of energized nanoclusters themselves results in contact with neighboring particles, and eventual merging. Such cluster merging is illustrated in Figure 4. Interestingly, Zoberbier et al. reported that clusters of 20-60 Os atoms inside carbon nanotubes continuously change their shape under the influence of an 80 keV electron beam, and bind strongly to the inner surface, weakening C-C bonds and promoting gradual removal of carbon atoms⁹.

Measurements of the length of the clusters indicate a linear relationship with time (Figure. 3g). This description is however only indicative due to the 3D nature of the nanocrystals. Significantly, this *in situ* generation of Os atoms on a self-supporting graphitic matrix produces 3D nanoclusters which are crystalline²⁹. This is illustrated by the fast Fourier transform (FFT) analysis (Figure 2h) of the ca. 1.5 nm-diameter Os nanocrystal depicted in Figure 2f. Figure 5 shows a montage of 10 osmium crystals along with their corresponding FFT analyses. In general, the Os crystals do not seem to have a simple hexagonal structure. Figure 6 shows two particles from the montage in Figure 5 with the closest appearance to hexagonal structure and compares them with simulations. The c-axis view is distinctive, and the a-axis view is a good fit, with the correct interatomic distances. Nevertheless, we believe that most of the images do not match either of these two views, which are not the only ones with views that look relatively simple. The other views have more complex behavior dependent on particle size and microscope focus. However, the average Os-Os distance measured over 85 different nanocrystals was determined to be 0.257 ± 0.019 nm, close to that in crystals of bulk osmium metal (0.27048 nm as the nearest neighbor distance at 293.15 K)^{30,31}. No change in Os-Os distance was observed during nanocrystal growth, as shown by the narrow standard deviation for the average Os-Os distance calculated from these 85 nanocrystals of various sizes (width between 1.5 and 2 nm).

Mixed Os/Ru nanocrystals

To demonstrate the generality of this new technology, we encapsulated 1 mol equiv of osmium complex **1** and 1 mol equiv of its ruthenium analogue [Ru(*p*-cymene)(1,2-dicarba-*c*-*closo*-dodecarborane-1,2-dithiolate)] in **RuOsMs** micelles, spread them onto a lacey carbon grid, and irradiated with the electron beam in a similar procedure as described above. Again, it was possible to observe metal atom migration and nanocrystal formation on a timescale of *ca.* 1 hour (Figure 7).

The composition of the crystals was analyzed by a combination of scanning-TEM (STEM) and energy-dispersive X-ray (EDX) analysis at the single particle level (Figure 8); this clearly demonstrated their hetero-metallic Ru/Os nature. Interestingly, the Ru/Os molar ratio determined for 55 different crystals ($0.91 \pm 0.07 / 1.13 \pm 0.07$) is very close to the initial Ru/Os ratio in the **RuOsMs** micelles determined by ICP-MS ($0.83 \pm 0.10 / 1.11 \pm 0.13$). This suggests that the atomic percentage of each metal in the nanocrystals can be readily tuned by varying the ratio of metal complexes encapsulated in the micelles, opening-up new perspectives for the design of hetero-metal nanocrystals with defined size and composition.

Discussion

We investigated the pattern and the rate of single Os movement by following the positions of a single Os atom over 200 seconds (20 frames with 10 s between each frame; see Figures 9c and 9d). Attempts were made to correlate the 'hopping' pattern with three different mechanisms: edge-to-edge, bridge-to-bridge, and hole-to-hole hopping over the hexagonal graphitic matrix (see Figures 9a and 9b). The closest fit corresponds to Os atoms moving from bridge-to-bridge (*i.e.* sitting between a pair of two adjacent atoms) at a rate of 0.0089 ± 0.0016 nm/s. Such a bridge localization of Os atoms is apparent in some HR-TEM pictures (see Figure 10), and is consistent with the favoured location of Pt atoms adsorbed on boron-doped graphene predicted by calculations¹⁸. Moreover, extrinsic point and line defects, such as foreign atoms at different positions, strongly modify the charge distribution and electronic structure of graphene³². DFT calculations have also suggested that graphitic boron dopants induce a deficiency of charge in graphene sheets, while sulfur doping of graphene is of particular interest as the resulting materials are expected to have a wider band gap than pure graphene³³. Boron-doped graphene films show a large number of Stone-Wales defects³⁴, while calculations indicate that sulfur-doping induces a large local curvature that tends to increase the local reactivity³⁵. Metal atoms have a high affinity for non-perfect and strained regions of point defects in graphene created by electron irradiation and annealing³⁶. Thus, boron and sulfur centers and the resultant defects

might act as centers which attract Os atoms. This was confirmed by HR-TEM images showing that Os atoms are located in disturbed zones of the hexagonal pattern of the matrix (see Figure 11). Individual Os atoms were also observed at step edges (Figure 1d); similar observations have been reported for Au and Pt atoms on graphene layers³⁷.

5 Such atom-by-atom fabrication of di- and poly-atomic molecules led to the rapid assembly of Os atoms into clusters. Figure 12 shows the atom-by-atom formation of osmium molecules, clusters made up of a few Os atoms, and nanocrystals. This appears to be the first observation of atom-by-atom fabrication of nanocrystals.

10 In conclusion, our synthetic technology provides a new route to the *in situ* generation of an unsupported graphitic matrix together with metal atoms which can migrate to form crystals. The method not only allows the multi-doping of the graphitic matrix, in this case with both boron and sulfur, but also capture of the dynamics of metal cluster formation in real space with atomic precision. Indeed, this first report of the use of block copolymer micelles to encapsulate metal
15 complexes for *in situ* reduction to metal atoms and formation of nanocrystals has allowed the dynamics of formation of metal nanocrystals to be observed, all the way from single atoms to molecules, clusters and then nanocrystals. This method has been exemplified by the production of a graphitic matrix doped with sulfur and boron, decorated with Ångstrom-sized crystals of osmium, opening-up possible new perspectives for the design of nanoscopic highly-dense and
20 pressure-resistant materials. The technology can readily be extended to expand the range of dopants in the supporting graphitic matrix, for example by replacing sulfur by selenium. It is also facile to fabricate a range of homo- and hetero-metal Ångstrom-size nanocrystals. We have illustrated this for mixed ruthenium-osmium crystals. Other combinations that might be readily accessible include Pt, Pd, Rh, Ir and Au, since the synthesis of precursor carborane complexes
25 of these metals is feasible. There is also wide scope for adapting this polymer-encapsulated metal complex synthetic procedure by variation of the block copolymer. The possibility of creating individual vacancies at desired locations in carbon nanotubes using electron beams has been recently demonstrated³⁸, and might also be combined with our procedure to allow the grafting of Os nanocrystals onto specific hotspots. Our synthetic route, which gives rise to a self-
30 supporting graphitic matrix, also offers attractive possibilities for studying the formation of multi-heteroatom-doped-graphitic sheets and the influence of dopants and defects without influence from underlying support grids (e.g. copper), a problem which often complicates the interpretation of metal deposition experiments. Finally, these nanocrystals may contribute to

conceptual advances in the design of a new range of nanodevices, for example for information storage, electronic circuitry, chemosensing and catalysis.

Methods

Materials

The preparation of the complex [Os(*p*-cym)(1,2-dicarba-*c*-oso-dodecaborane-1,2-dithiolato)] (**1**) was based on a previous report²³. The triblock copolymer P123 [poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol)] was purchased from Sigma-Aldrich and used as received. Anhydrous tetrahydrofuran (Aldrich) was used. 18.2 mega-ohm purity water was collected from a Purelab[®] UHQ USF Elga system. Holey carbon grids with 200 mesh and lacey carbon grids were purchased from Quantifoil Micro Tools GmbH and Elektron Technology UK Ltd, respectively and used as received.

Synthesis of OsMs and OsRuMs

A tetrahydrofuran (THF) solution (1 mL) of complex **1** (5 mg/mL) was added to an aqueous solution (10 mL) of polymer P123 (5 mg/mL) and the resultant mixture was stirred at ambient temperature for 4 h. The solution was then dialyzed to remove the THF (MWCO = 1000 Da), for 48 h, and then freeze-dried. A similar procedure was used for synthesizing **OsRuMs** with 1 mol equiv of **1**, 1 mol equiv of the Ru analogue and 1 mol equiv of polymer P123.

Characterization of the micelles OsMs and P123Ms

UV-vis spectra (Figure 13) and dynamic light scattering (DLS) experiments (Figure 14) unambiguously demonstrated that polymer P123 and complex **1** self-assemble in aqueous solution. Encapsulation decreased the size of P123Ms micelles from 19.6±1.80 nm (hydrodynamic diameter, D_h) to 11.5±2.35 nm for **OsMs** with a dispersity ($\mathcal{D}$) of 0.03 (Figure 14a; Table 1). Although micellar size usually increases after encapsulation of organic molecules³⁹, incorporation of hydrophobic molecules can result in expulsion of water from the micelles, causing a contraction⁴⁰. The hydrophobicity of **1** probably results in a stronger folding of the PPO chains around the complex through hydrophobic interactions, with concomitant expulsion of water from the core. A small second population of **OsMs** particles (<0.01 % in number) was found at $D_h \sim 220$ nm, exhibiting a strong intensity in DLS analysis, due to the aggregation of some particles (Figure 14c).

Cryogenic TEM analysis without staining was then performed on Quantifoil[®] carbon-coated grids to observe the morphology of the hydrophobic core (containing osmium complexes) of the

nanoparticles in solution. The high contrast provided by the heavy osmium centers allowed facile imaging of the osmium-PPO core, but impaired the observation of the PEO corona due to the polymer hydrated state; and disfavored by the small diameter of the micelles (Figure 15a), even after attempts to further stain the samples with uranyl acetate. From these experiments, it was clear that spherical micellar morphologies are formed when polymer P123 encapsulates complex 1. The observed diameter of these **OsMs** nano-spheres is 7.85 ± 1.97 nm (Figure 15b) with very low close-to-ideal dispersity, based on 157 particles counting (1.06; 1.00 being for ideal mono-disperse systems; see Table 1). These data are in accordance with the hydrodynamic diameters determined by DLS within experimental error.

To gain further insight into their structures in aqueous solution, and to confirm cryo-TEM and DLS results, **OsMs** and P123Ms were analyzed by small-angle X-ray scattering (SAXS; Figure 16). The experimental profiles were fitted to three model functions for spherical micelles: SphereForm, CoreShellSphere, and PolyCoreShellRatio (PCR). The PCR model fitted excellently for both micelles with very low dispersity parameters (0.161 for **OsMs** and 0.146 for P123Ms, 0 being an ideal mono-disperse system, Table 1). These analyses demonstrated that **OsMs** self-assembly leads to core/shell micelles with a core diameter of 9.06 ± 0.12 nm, and a shell diameter of 6.50 ± 0.15 nm (Table 1). The core dimension of **OsMs** was larger than for P123Ms (6.74 ± 0.06 nm), whilst the corona dimension of **OsMs** was smaller than for the P123Ms shell (12.22 ± 0.17 nm). The diameters of **OsMs** micelles by DLS and cryo-TEM are in accordance with the core diameter determined by SAXS within the experimental errors, while the diameters of P123 micelles from DLS and SAXS studies are similar.

From these data (scattering length density calculations, degrees of polymerization of Pluronic® P123, and the molecular formulae of the polymer and of complex 1; see Instrumentation and Methods), aggregation numbers for **OsMs** and P123Ms micelles were determined as 20 ± 2 monomer chains per P123Ms micelle and 52 ± 6 monomer chains per **OsMs** micelles. Determinations of osmium by inductively coupled plasma mass spectrometry (ICP-MS) gave a polymer/complex 1 ratio of $1/1 \pm 0.091$ for **OsMs** showing that the 52 chains polymer chains self-assembled with 52 ± 11 complexes 1 (see Table 1). Similar core/shell diameters (Table 1) with excellent fits to the PCR model were obtained from experiments at three different concentrations (1, 5, 10 mg/mL; Supplementary Figure 17a and 17b) for both **OsMs** and P123Ms. Hence concentration does not influence the micellar structure, a parameter of importance for Pluronic®-type self-assemblies.

Furthermore, dry-state TEM images (see Figure 18) demonstrate that the **OsMs** micelles form stable nanostructures in the dry state.

Instrumentation

UV-visible spectroscopy: UV-visible absorption spectra were recorded on a temperature-controlled Varian CARY 300 Biospectrophotometer using 1-cm path-length quartz cuvettes (0.5 mL).

Inductively coupled plasma mass spectrometry: Osmium (^{189}Os) content was determined using an ICP-MS Agilent technologies 7500 series instrument. The standard for osmium was purchased from Aldrich. Calibration curves were prepared using Os standard solutions in double deionised water (ddw) with 3% nitric acid, ranging between 50 and 0.5 ppb (9 points). Samples were freshly prepared in ddw with 3% nitric acid. Readings were made in no-gas mode with a detection limit of 1 ppt for ^{189}Os .

Dynamic light scattering DLS: The hydrodynamic diameter (D_h) of nanoparticles was determined by dynamic light scattering (DLS). Typically, an aqueous nanoparticle solution was measured with a Malvern Zetasizer NanoS instrument equipped with a 4 mW He-Ne 633 nm laser module at 25 °C. Measurements were carried out at a detector angle of 173° (back scattering). Data were analyzed by the Malvern DTS 6.20 software. D_h was calculated by fitting the apparent diffusion coefficient in the Stokes-Einstein equation $D_h = kT / (3\pi\eta D_{app})$, where k is the Boltzmann constant, T is the temperature and η is the viscosity of the solvent. D_h coincides with the hydrodynamic diameter when the sample is made of monodispersed spherical particles (D_{app} equals the translational diffusion D_t).

Transmission electron microscopy TEM: TEM was performed using a JEOL 2000FX at 200 kV. TEM samples were prepared by using holey and lacey carbon grids. One drop of the sample solution (5 μL) was applied to the grid and after 2 min the solution was blotted away before drying. Images were recorded on a Gatan Orius camera and were analyzed using ImageJ software. At least 100 particles from different parts of the grid were counted for each sample to obtain the average diameter.

Cryogenic electron microscopy cryo-TEM: A JEOL 2010F TEM was operated at 200 keV and images were recorded on a Gatan UltraScan 4000 camera for cryo-TEM and glow discharge. The samples were prepared at ambient temperature by placing a droplet on a TEM grid. The extra liquid was then blotted with a filter paper and the grid was inserted in liquid ethane at its freezing point. The frozen samples were subsequently kept under liquid nitrogen.

High resolution electron microscopy HR-TEM: A JEOL JEM-ARM200F HR-TEM was operated at 80 keV, 1.9 pA/cm², with spherical aberration (C_s) tuned to approximately +1 μm and images were recorded on a Gatan SC1000 Orius CCD camera.

Small-angle X-ray scattering (SAXS): Measurements were carried out on the SAXS beamline at the Australian Synchrotron facility at a photon energy of 11 keV. The samples in solution were in 1.5 mm diameter quartz capillaries. The measurements were collected at a sample to detector distance of 3.252 m to give a q range of 0.004 to 0.2 Å⁻¹, where q is the scattering vector and is related to the scattering angle (θ) and the photon wavelength (λ) by the following equation (1):

$$(1) \quad q = \frac{4\pi \sin(\theta)}{\lambda}$$

The scattering from a blank (H₂O) was measured in the same location as sample collection and was subtracted for each measurement. Data were normalized for total transmitted flux using a quantitative beamstop detector and absolute scaled using water as an absolute intensity standard. The two-dimensional SAXS images were converted in one-dimensional SAXS profiles ($I(q)$ versus q) by circular averaging, where $I(q)$ is the scattering intensity. Functions were used from the NCNR package. Scattering length densities were calculated using the "Scattering Length Density Calculator" provided by NIST Center for Neutron Research.

We decided to conduct further experiments to determine the effect that the dopant atoms have on mobility of atoms located on a graphitic substrate.

We synthesized two graphenic surfaces for our experiments. The first was doped with hetero-atoms boron and sulfur (B/S) following the procedure we described above while the second was doped with hetero-atoms boron and selenium (B/Se). This involved irradiating **OsMs-Se** micelles made of [Os(*p*-cymene)(1,2-dicarba-*c*/oso-dodecarborane-1,2-diselenate)] encapsulated in tri-block copolymer P123 with the electron beam of an aberration-corrected TEM-STEM with a Schottky thermal field-emission source (80 keV; 1.9 pA/cm² or 7.6×10⁷ electrons·nm⁻²·s⁻¹). In general there were regions of the surface which were single-layer and on which an idealized hexagonal lattice could be readily overlaid, although the surface was clearly inhomogeneous in some regions as expected from the presence of the B/S and B/S dopants. The presence of boron and chalcogen atoms as well as osmium was confirmed by a combination of energy-dispersive X-ray (EDX) analysis, and electron energy loss spectroscopy of energy filtered TEM (EFTEM).

We investigated single atom migration by following the positions of individual Os atoms on B/S (over 390 seconds; 40 frames with 10 s between each frame) and B/Se surfaces (over 15 seconds; 31 frames with 0.5 s between each frame). The positions of each atom were extracted from a series of images from 3 different areas of the grid. Successive images were aligned and

the drift was compensated by using the Plugin StackReg in Fiji-ImageJ, and by using a Digital Micrograph(TM) script.

Fig. 19(a) shows an example of experimental TEM images and the trajectory of an individual Os atom on the B/S surface recorded at different irradiation times (5 frames extracted from a total of 40 pictures over a total irradiation time of 390 s). Figs. 19(b) and 19(c) show the illustrative trajectories of three individual osmium atoms on the B/S- and B/Se-doped graphenic surfaces, respectively. Owing to the high contrast of osmium atoms as compared to the graphenic surfaces, the extraction of the coordinates of the atom in each frame is readily achieved from a 3D surface projection for each TEM picture (Fig. 19(a)).

The experimental images also clearly highlight the existence of a number of anchoring points on both surfaces, positions of apparent long residence times (Fig. 19). The analysis of the various trajectories suggest that the chalcogen atoms themselves induce the differences in atomic migration, and have a direct impact on the trajectory of osmium atoms on the surface. This might involve direct Os-chalcogen binding, but the effects could also be propagated over a longer distance on the conjugated graphenic lattice. Interestingly, Cretu *et al.*⁴¹ have reported experimental observations of the migration of individual tungsten atoms on a graphitic surface and shown that W atoms are mobile but can be trapped by defective sites. They showed that below 250 °C, when the graphene lattice was heavily damaged by the beam, almost no jumps occurred and the W atoms were pinned by larger irradiation-induced lattice defects. In the range 250 – 500°C, jumping of W atoms was observable, and escape from a trapping centre could be induced thermally or by electron irradiation, a combination of thermal and beam effects which explains the observed small oscillations. In related work the same group observed the trapping of Mo atoms at defect sites in carbon nanotubes and in graphene⁴² and recently Pb and Te atoms have been trapped on amorphous graphene and at edge sites of holes in graphene.⁴³ Our experimental data are consistent with these previous observations and also show that such an escape by Os atoms from anchoring sites, at a temperature close to ambient, is dependent on the nature of the graphenic dopants.

We determined the apparent rate of migration of individual osmium atoms on the two multi-doped graphenic surfaces (average calculated from observation of 10 single atoms). It should be noted that the real speed of motion of the atoms is at least the apparent monitored rate of migration, since we are limited by the speed of the camera and there could be more steps at intermediate times between frame captures. Fig. 19(d) shows the dependence of the cumulative path length covered by two individual Os atoms (blue: B/Se surface; yellow: B/S surface) on

irradiation time on the two surfaces. Remarkably, the chalcogen dopant (S vs. Se) dramatically influences the apparent rate of migration. The Os atom travels an apparent distance of 3.5 nm in 15 s on the B/Se surface, while the same distance is covered by the Os atom in 390 s on the B/S surface. This *ca.* 26 $\times$ higher speed of Os atoms on the B/Se surface compared to the B/S surface (0.233 $\pm$ 0.034 nm/s versus 0.0089 $\pm$ 0.0019 nm/s) is illustrated in Fig. 19(e). It also appears that on both surfaces, the apparent rate of migration is not constant, but varies over time, with significant autocorrelation (Figs. 19(e) and 19(f)). This confirms the existence of anchors and suggests that the atom must receive a minimum energy from the high-energy electron beam to be able to move from an anchoring site to another adjacent position. Thus, by determining the time of irradiation needed to observe a jump from an anchor to another site, directly from the HR-TEM images, we found that an individual Os atom was irradiated for 70 $\pm$ 9 seconds on the B/S surface before hopping to another site. On the B/Se surface, an individual Os atom hopped to another site after irradiation for only *ca.* 1.5 $\pm$ 0.3 seconds.

We also investigated the dynamics of migration of two close Os atoms on the B/S and B/Se surfaces. Using the same procedure as for individual atoms, we elucidated the trajectory of each atom (Fig. 20(a)) and thus the trajectory of the pair (Figs. 20(b) and 20(c)). The atomic positions were extracted from a series of time-lapse TEM images, as for individual atoms. Notably, the average Os-Os distance of 0.284 $\pm$ 0.077 nm on the B/Se surface and 0.243 $\pm$ 0.059 nm on B/S are both close to the Os-Os distance in metallic Os (0.27048 nm as the nearest neighbor distance at 20 °C)^{44,45} suggesting that these two Os atoms form a true Os₂ diatomic molecule. Furthermore, the two close Os atoms undergo concerted migration on the multi-doped graphenic surfaces. The dependence of the jumping pattern for each Os atom shown in Fig. 20(c) on irradiation time is shown in Fig. 20(e), and suggests that the two atoms are indeed bonded and behave as a single entity and not as two isolated atoms on the surface. Similar to the movement of isolated individual Os atoms, the distance travelled by each atom of the Os₂ molecule increases linearly with irradiation time on both surfaces (Fig. 20(d)). The average apparent rate of migration of an Os₂ diatomic molecule was found to be slightly slower than for individual Os atoms on both B/S and B/Se surfaces (0.0074 $\pm$ 0.0028 nm/s, and 0.151 $\pm$ 0.045 nm/s, respectively). Again, as for single Os atoms, the apparent rate of migration of Os₂ on the B/Se-doped surface was dramatically faster (*ca.* 20 $\times$) than on the B/S-doped surface. We also note that defects within graphenic layers can themselves migrate under the influence of an electron beam⁵⁶ Although such effects can be quantified on pure graphene, they are more difficult to map on heavily doped lattices such as those studied here. It should be borne in mind

however that such movements of carbons or dopants within the support layer could also influence the movement of Os atoms, as is apparent in Fig. 20(a).

Discussion

5 Understanding the fundamental mechanisms of interactions between incident electrons and atoms/molecules provides unique information on the chemical structure of a variety of systems⁴⁷ To gain more information on the mechanism of hopping of individual osmium atoms on the B/S and B/Se doped graphenic surfaces, we have investigated whether the Os atoms follow Brownian Motion (BM). In BM, each jump is independent and identically distributed according to
10 a normal distribution with variance proportional to the time between observations, so we looked for evidence of this in the data, consisting of the migration of 5 Os atoms on each kind of surface. First we checked that the size of the jumps in the x and y directions were the same, pooling together all of the jumps for the 5 separate atoms. There appeared to be no significant difference in the dynamics of migration on the sulfur-doped surface and only a very small
15 difference on the selenium-doped surface. The histograms shown in Figs. 21(a) and 21(b) were observed to be similar, and as such x and y jumps were pooled together for further analysis. We also assumed that the Os atoms were not drifting in any particular direction and so the mean jump would be zero, which also appeared to be confirmed by the data. Next, we fitted a Gaussian density to the pooled jump data and plotted a normal Quantile-Quantile plot to assess
20 deviations from normality (Figs. 21(c) and 21(d)). It is clear from these plots that there are more long-range jumps than would be expected for a Brownian Motion, but for completeness we also performed a Shapiro-Wilk test of normality⁴⁸ both the selenium- and sulfur-pooled data gave p-values below 0.001 and so we can reject the hypothesis that Brownian Motion describes the movement of the Os atoms. Returning to the raw data, we see that no large jumps are captured
25 for these two atoms. It is clear from Table S3 that the jump sizes are larger on selenium-doped than on sulphur-doped graphene, but it is nonetheless interesting to investigate whether they come from the same distribution. Although there is a small amount of deviation from the line in the lower tail, the plot does suggest that the distributions are indeed very similar.

In conclusion, the new generations of electron microscopes with their atomic resolution
30 capability and ultra-fast cameras offer the possibility of imaging dynamic processes in real time. However, there is currently little reported data on such dynamic interactions at the level of the individual atom, owing, in particular, to the fast migration of single atoms on graphene. Here, we have used a new synthetic methodology for the *in situ* formation of graphenic surfaces doped

with boron and sulfur (B/S) or selenium (B/Se) hetero-atoms. The doping creates anchoring points for individual Os atoms, slowing down their migration so that it is commensurate with the timescale of image capture on an aberration-corrected transmission electron microscope. We have imaged in real time the migration of individual Os atoms on these surfaces, and this has
5 provided unprecedented experimental data on the dynamic behavior of individual atoms without intervention using physical probes. We have shown that Os atoms move *ca.* 26× faster when S is substituted by Se (0.0089 ± 0.0020 vs 0.233 ± 0.034 nm/s). Os₂ dimers, as expected, move more slowly than single Os atoms, but the S/Se difference in speed is similar (20×: 0.0074 ± 0.0028 vs 0.151 ± 0.045 nm/s). Indirectly, through choice of the dopants, our
10 methodology can provide control of atomic dynamics and might lead to a wide range of potential applications (e.g. patterning on surfaces, security labelling at the atomic level, sealing confidential documents).

We believe that a larger range of new doped-graphenic matrices (that could further modify the migration rates) is possible (including without limit the other chalcogens and/or those species
15 studied by *Cretu*⁴¹ including Mo, W, Pb, Te), and that the deposition of other metal atoms (e.g. other precious metals such as Au, Pt, and Pd) is possible using our methodology and that our methodology will help aid, perhaps with computational studies, in the fundamental understanding of these dynamic processes.

Metal nanocrystals have raised considerable expectations for application in healthcare⁴⁹⁻⁵¹
20 electronics,⁵² and other areas. Their dimensions (1 – 100 nm) lead to physical and chemical properties that differ from those of bulk materials. Methods for fabricating nanocrystals are generally divided into two main approaches: top-down methods and bottom-up methods.⁵³ The former relies on a progressive removal of material until the desired nanomaterial is obtained⁵⁴ whilst the latter uses atomic or molecular precursors and gradually assembles them until the
25 desired structure is formed.⁵⁵ Both methods requisite a careful control of the fabrication conditions and of the environment conditions, and follow a three-stage approach: nucleation, evolution of nuclei into seeds, and growth of seed into nanocrystals.⁵⁶ Nucleation is the first step of any crystallisation process, and understanding this phenomenon is of utmost importance not only in biochemistry – nucleation of bubbles in DNA for replication and transcription,
30 crystallization of proteins, replication of viruses – but also in materials science and in physics – e.g. crystal growth of metal nanocrystals and nanoparticles. Nonetheless, the observation of this first stage is particularly challenging, owing to experimental limitations for identifying, capturing, and observing in real-time the dynamics of nucleation from individual atoms to small clusters of only a few atoms, to nanocrystals.

The methodology detailed herein involves irradiation, for example high-energy electron beam irradiation, of metallated micelles, for example using an aberration-corrected high-resolution transmission electron microscope (AC-TEM). Upon irradiation, the micelles form a doped graphenic support on which individual osmium atoms hop and migrate to form nanocrystals, as small as 15 Å in diameter in less than 1 hour. Crystal growth was observed, quantified and controlled in real time. As an application of this technology, we report here the kinetics of gold, osmium, ruthenium, and iridium nanocrystal formation from individual atoms to nuclei – minuscule clusters made of a very few atoms formed in the earliest stage of a nanocrystal synthesis.

Results

We synthesized four metallated micellar formulations for our experiments (Figure 22), and irradiated them with the electron beam of an aberration-corrected TEM-STEM with a Schottky thermal field-emission source (80 keV; 1.9 pA/cm² or 7.6×10⁷ electrons·nm⁻²·s⁻¹). The **OsMs** and **RuMs** micelles made of [Os/Ru(*p*-cymene)(1,2-dicarba-*c*-*closo*-dodecarborane-1,2-dithiolate)] encapsulated in tri-block copolymer Pluronic® P123 were synthesized following the procedure we described recently,^{57,58} while the gold-containing **AuMs** and iridium-containing **IrMs** micelles, made of [Au(1,2-dicarba-*c*-*closo*-dodecarborane-1,2-dithiolate)₂] and [IrCp*(1,2-dicarba-*c*-*closo*-dodecarborane-1,2-dithiolate)], respectively, were new. Upon irradiation, each micellar system was degraded by the electron beam, the polymer decomposing into a boron- and sulfur-doped graphenic surface, and the metal atoms being reduced in individual atoms hopping on the surface.

In order to first ensure that the micelle degradations lead to the formation of metal nanocrystals for each metal, we irradiated the TEM grids for up to 150 min. We obtained reproducible results with similar crystal formation for the ruthenium, iridium, and gold systems. Measurements of the length of the atomic aggregates indicate a linear relationship with time (between 1 and up to 105 minutes) in the four cases (Figure 23). The composition of the crystals was analyzed by a combination of scanning-TEM and energy-dispersive X-ray analysis at the single particle level, which clearly demonstrated their metallic nature. Electron energy loss spectroscopy also suggested that boron and sulfur from the carborane ligand in the metallated micelle precursors are present in the graphenic matrix. These results allowed us to generalize our recently reported methodology to other precious metals than osmium, and demonstrate its potential for the design of ultra-small nanocrystals with possible usefulness in the design of a new range of nanodevices, for example, for chemosensing (gold) and catalysis (ruthenium, iridium).

To gain more information on the nucleation stage of these nanocrystal formations, we then studied the early steps of nuclei aggregation for each metal. The metal-metal distances for Au, Os, Ir, and Ru were first measured on small molecules of only two atoms on the surface. These average Os–Os, Au–Au, Ir–Ir, and Ru–Ru distances were measured over 30 different clusters and were determined to be close to that in crystals of respective bulk metal. Furthermore, no change in metal–metal distance was observed during nanocrystal growth, suggesting that there is no intercalation of any hetero-atom (B, S, or O) between the metal atoms during nucleation (Figure 24).

Conclusions

Nucleation is the first stage of any crystallisation process. Understanding nucleation is of utmost importance in biology, physics, and chemistry. In materials science in particular, achieving kinetic control of the nucleation of nanocrystals and nanoparticles would open-up new perspective to precisely tailor such objects and therefore to fully exploit their unique physical and chemical properties. However, observing, identifying, and capturing in real-time and in real-space the dynamics of nucleation from individual atoms to small clusters of only a few atoms, and to nanocrystals is an experimental frontier. Here, based on our recently developed new methodology, we report for the first time the kinetics parameters of precious metal (gold, iridium, osmium, and ruthenium) nucleation. We anticipate that nanocrystallometry will open-up new perspective for studying the nucleation process of a number of chemical systems. We further anticipate that other complexed metals will be susceptible to nanoparticle formation using our methodology.

Different Substrates

In order to determine the effect of the effect of the underlying substrate on nanocrystal growth we applied the osmium micelles to a silicon nitride membrane and irradiated as per Figure 1 and the above description.

Preliminary observations

- The micelles spread less on the silicon nitride membrane than on the lacey carbon grid. As a consequence, the nanocrystals will be produced in smaller areas, and therefore are formed quicker on silicon membranes than on lacey carbon grids.

- With this surface, it seems to be possible to burn the graphenic matrix in order to only have the nanocrystals on the silicon nitride surface.

Preparation of the samples

- 5 0.1 μL of complex in polymer at 1 mg/mL was deposited on the window and left to dry overnight.

Window: silicon nitride membrane, membrane size: 0.5 mm x 0.5 mm, membrane thickness: 20 nm, Silson ref: 11503103

Observation of the window on the 2100 HR-TEM (21.2 pA/cm² at 300k):

- 10 Presence of big morphologies all over the grid. Area 1: magnification from 15k to 300k – timescale 0 to 20 minutes of irradiation.

The results, to be viewed in concert with Figure 25 (in sequence as a to g), were as follows:

Irrad. Time (min)	Comment and Observations
1	The micelles made of P123 polymer spread on the surface to form shown type of morphologies
3	
5	Already some darker areas visible
10	Darker areas more visible, look similar to what has been previously observed on lacey carbon TEM grids
15	Different size of clusters, some with atoms almost visible and aligned. Formation of these big clusters seems to be faster than on lacey carbon TEM grids
17	
20	When magnification is low again, the size morphology is still the same, but some areas are less dark which means a loss of materials (matrix burnt).

15

The experiments demonstrate that continued irradiation has the effect of pyrolysing or other removing the carbon graphitic structure, thereby demonstrating that it is possible to provide nanocrystals on a silicon nitride substrate at very quick rates in a controlled manner, due to the lack of spread of the micelles.

20

Methods of nanocrystal formation

In the above description we discuss the use of electron beam irradiation to generate the nanocrystals. We have now further investigated two new irradiation methodologies, as follows:

25

Laser irradiation.

The experimental setup of the light irradiation source is as follows:

A commercially available Ti:sapphire oscillator and regenerative amplifier system (femtosecond laser Spectra-Physics XP Tsunami and Spitfire XP, respectively) produce 3 mJ laser pulses of
5 ≈ 40 fs duration centered around 800 nm at a repetition rate of 1 kHz. The sample was exposed to $\frac{1}{3}$ of the fundamental [0.5 mJ pulses] for 1, 2 and 5 hours.

The osmium micelles as formed in accordance with the above description and shown in Figure 1 were irradiated using the above-described laser apparatus.

Some TEM images obtained after 1 hour of laser irradiation are shown in Figure 26.

Microwave irradiation.

A Discover® SP system microwave has been used to irradiate a solution of osmium metallated precursors (formed in accordance with the above description and as shown in Figure 1) with a program heating up to 140 °C and by applying a power of 150 W for 10 min (with a pressure of
15 250 PSI). This leads to the formation of narrowly distributed Os nanocrystals, as shown in Figure 27.

These experiments clearly show that laser and microwave irradiation are effective in the formation of metal nanocrystals and provides evidence that a broad range of energetic
20 irradiation of labile metal complexes can be utilised in the controlled formation metal nanocrystals.

The data herein clearly demonstrates that using our methodology it is possible to form a broad range of metal nanocrystals (on a graphitic substrate on a variety of supports) in a highly
25 controlled manner, using a broad range of techniques to energise the material. Moreover, we believe that this methodology will open up new avenues for the manufacture of nanoparticle devices with novel and designed metal mixing ratios and can be achieved using readily available equipment under both oxidizing and non-oxidising conditions. We believe that this opens up a range of possibilities in the fabrication of new devices with bespoke, designed
30 properties.

References

- 1 Amoretti, M. *et al.* Production and detection of cold antihydrogen atoms. *Nature* **419**, 456-459 (2002).
- 5 2 Arvizo, R. R. *et al.* Intrinsic therapeutic applications of noble metal nanoparticles: past, present and future. *Chem. Soc. Rev.* **41**, 2943-2970 (2012).
- 3 Forster, S., Meinel, K., Hammer, R., Trautmann, M. & Widdra, W. Quasicrystalline structure formation in a classical crystalline thin-film system. *Nature* **502**, 215-218 (2013).
- 4 Ibáñez, M. & Cabot, A. All Change for Nanocrystals. *Science* **340**, 935-936 (2013).
- 10 5 Hunt, L. B. The True Story of Purple of Cassius. *Gold Bull.* **9**, 134-139 (1976).
- 6 Faraday, M. Experimental Relations of Gold (and Other Metals) to Light. *Philos. Trans. R. Soc. London* **147**, 145-181 (1857).
- 7 Rao, C. N. R., Thomas, P. J. & Kulkarni, G. U. *Nanocrystals: Synthesis, Properties and Applications*. Vol. 95 (Springer-Verlag 2007).
- 15 8 Qi, X. *et al.* In Situ Modification of Three-Dimensional Polyphenylene Dendrimer-Templated CuO Rice-Shaped Architectures with Electron Beam Irradiation. *J. Phys. Chem. C* **114**, 13465-13470 (2010).
- 9 Zoberbier, T. *et al.* Interactions and Reactions of Transition Metal Clusters with the Interior of Single-Walled Carbon Nanotubes Imaged at the Atomic Scale. *J. Am. Chem. Soc.* **134**, 3073-3079 (2012).
- 20 10 Bragg, W. L. Diffraction of X-rays by crystals. *Nobel Lecture, Physics 1901-1921*, Elsevier Publishing Company, Amsterdam, 1967.
- 11 Oh, M. H. *et al.* Galvanic Replacement Reactions in Metal Oxide Nanocrystals. *Science* **340**, 964-968 (2013).
- 12 Yamada, Y. *et al.* Nanocrystal bilayer for tandem catalysis. *Nat. Chem.* **3**, 372-376 (2011).
- 25 13 Yang, J., Sargent, E., Kelley, S. & Ying, J. Y. A general phase-transfer protocol for metal ions and its application in nanocrystal synthesis. *Nat Mater* **8**, 683-689 (2009).
- 14 Langille, M. R., Personick, M. L. & Mirkin, C. A. Plasmon-Mediated Syntheses of Metallic Nanostructures. *Angew. Chem. Int. Ed.* **52**, 13910-13940 (2013).
- 15 Lara, P., Philippot, K. & Chaudret, B. Organometallic Ruthenium Nanoparticles: A Comparative Study of the Influence of the Stabilizer on their Characteristics and Reactivity. *ChemCatChem* **5**, 28-45 (2013).
- 30 16 Xia, Y., Xiong, Y., Lim, B. & Skrabalak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angew. Chem. Int. Ed.* **48**, 60-103 (2009).
- 17 Lee, J., Zhou, W., Pennycook, S. J., Idrobo, J.-C. & Pantelides, S. T. Direct visualization of reversible dynamics in a Si₆ cluster embedded in a graphene pore. *Nat. Commun.* **4**, 1650 (2013).
- 35 18 Muhich, C. L., Westcott, J. Y., Morris, T. C., Weimer, A. W. & Musgrave, C. B. The Effect of N and B Doping on Graphene and the Adsorption and Migration Behavior of Pt Atoms. *J. Phys. Chem. C* **117**, 10523-10535 (2013).
- 19 Zhang, T., Zhu, L., Yuan, S. & Wang, J. Structural and Magnetic Properties of 3d Transition-Metal-Atom Adsorption on Perfect and Defective Graphene: A Density Functional Theory Study. *ChemPhysChem* **14**, 3483-3488 (2013).
- 40 20 Lazar, P. *et al.* Quantification of the Interaction Forces between Metals and Graphene by Quantum Chemical Calculations and Dynamic Force Measurements under Ambient Conditions. *ACS Nano* **7**, 1646-1651 (2013).
- 21 *CRC Handbook of Chemistry and Physics*. (CRC Press, 2011).
- 45 22 Chamberlain, T. W. *et al.* Formation of uncapped nanometre-sized metal particles by decomposition of metal carbonyls in carbon nanotubes. *Chem. Sci.* **3**, 1919-1924 (2012).
- 23 Herberhold, M., Yan, H. & Milius, W. The 16-electron dithiolene complexes (p-cymene)M[S₂C₂(B10H10)] (M=Ru, Os) containing both η⁶-(p-cymene) and η²-(ortho-carborane-dithiolate): adduct formation with Lewis bases, and X-ray crystal structures of (p-cymene)Ru[S₂C₂(B10H10)](L) (L=PPh₃) and {(p-cymene)Ru[S₂C₂(B10H10)]}₂(μ-LL) (LL=Ph₂PCH₂CH₂PPh₂ and N₂H₄). *J. Organomet. Chem.* **598**, 142-149 (2000).
- 50 24 Scholz, M. & Hey-Hawkins, E. Carboranes as Pharmacophores: Properties, Synthesis, and Application Strategies. *Chem. Rev.* **111**, 7035-7062 (2011).
- 25 Pitto-Barry, A. & Barry, N. P. E. Pluronic® block-copolymers in medicine: From chemical and biological versatility to rationalisation and clinical advances. *Polym. Chem.*, DOI:10.1039/C1034PY00039K (2014).
- 55 26 Kiss, É., Keszthelyi, T., Kormány, G. & Hakkel, O. Adsorbed and Spread Layers of Poly(ethylene oxide)-Poly(propylene oxide)-Poly(ethylene oxide) Block Copolymers at the Air-Water Interface Studied by Sum-Frequency Vibrational Spectroscopy and Tensiometry. *Macromolecules* **39**, 9375-9384 (2006).
- 27 Suenaga, K. & Koshino, M. Atom-by-atom spectroscopy at graphene edge. *Nature* **468**, 1088-1090 (2010).
- 60 28 Wang, H. *et al.* Interaction between single gold atom and the graphene edge: A study via aberration-corrected transmission electron microscopy. *Nanoscale* **4**, 2920-2925 (2012).

- 29 Online Dictionary of CRYSTALLOGRAPHY. <http://reference.iucr.org/dictionary/Crystal>, Crystal Definition (2012).
- 30 Swanson, H. E., Fuyat, R. K. & Ugrinic, G. M. *Standard X-Ray Diffraction Powder Patterns in National Bureau of Standards Circular*. Vol. IV (1955).
- 5 31 Arblaster, J. W. Densities of Osmium and Iridium. *Platinum Metals Rev.* **33**, 14-16 (1989).
- 32 Banhart, F., Kotakoski, J. & Krasheninnikov, A. V. Structural Defects in Graphene. *ACS Nano* **5**, 26-41 (2010).
- 33 Poh, H. L., Šimek, P., Sofer, Z. & Pumera, M. Sulfur-Doped Graphene via Thermal Exfoliation of Graphite Oxide in H₂S, SO₂, or CS₂ Gas. *ACS Nano* **7**, 5262-5272 (2013).
- 10 34 Zhao, L. *et al.* Local Atomic and Electronic Structure of Boron Chemical Doping in Monolayer Graphene. *Nano Lett.* **13**, 4659-4665 (2013).
- 35 Garcia, A. G., Baltazar, S. E., Castro, A. H. R., Robles, J. F. P. & Rubio, A. Influence of S and P Doping in a Graphene Sheet. *J. Comput. Theor. Nanos.* **5**, 2221-2229 (2008).
- 36 Cretu, O. *et al.* Migration and Localization of Metal Atoms on Strained Graphene. *Phys. Rev. Lett.* **105**, 196102 (2010).
- 15 37 Gan, Y., Sun, L. & Banhart, F. One- and Two-Dimensional Diffusion of Metal Atoms in Graphene. *Small* **4**, 587-591 (2008).
- 38 Rodríguez-Manzo, J. A. & Banhart, F. Creation of Individual Vacancies in Carbon Nanotubes by Using an Electron Beam of 1 Å Diameter. *Nano Lett.* **9**, 2285-2289 (2009).
- 20 39 Jansson, J., Schillén, K., Olofsson, G., Cardoso da Silva, R. & Loh, W. The Interaction between PEO-PPO-PEO Triblock Copolymers and Ionic Surfactants in Aqueous Solution Studied Using Light Scattering and Calorimetry. *J. Phys. Chem. B* **108**, 82-92 (2003).
- 40 Parmar, A., Aswal, V. K. & Bahadur, P. Interaction between the ionic liquids 1-alkyl-3-methylimidazolium tetrafluoroborate and Pluronic® P103 in aqueous solution: A DLS, SANS and NMR study. *Spectrochim. Acta Mol. Biomol. Spectros.* **97**, 137-143 (2012).
- 25 41. O. Cretu, A. V. Krasheninnikov, J. A. Rodríguez-Manzo, L. Sun, R. M. Nieminen and F. Banhart, *Phys. Rev. Lett.*, 2010, **105**, 196102.
42. J. A. Rodríguez-Manzo, O. Cretu and F. Banhart, *ACS Nano*, 2010, **4**, 3422-3428.
43. C. Gong, A. W. Robertson, K. He, C. Ford, A. A. R. Watt and J. H. Warner, *Dalton Trans.*, 2014, **43**, 7442-7448.
- 30 44. H. E. Swanson, R. K. Fuyat and G. M. Ugrinic, *Standard X-Ray Diffraction Powder Patterns in National Bureau of Standards Circular*. 1955.
45. J. W. Arblaster, *Platinum Metals Rev.*, 1989, **33**, 14-16.
46. J. Kotakoski, C. Mangler and J. C. Meyer, *Nat Commun*, 2014, **5**, 4991.
- 35 47. T. W. Chamberlain, J. Biskupek, S. T. Skowron, P. A. Bayliss, E. Bichoutskaia, U. Kaiser and A. N. Khlobystov, *Small*, 2014.
48. S. S. Shapiro and M. B. Wilk, *Biometrika*, 1965, **34**, 591611.
49. E.-K. Lim, T. Kim, S. Paik, S. Haam, Y.-M. Huh and K. Lee, *Chem. Rev.*, 2014.
50. J. Yao, M. Yang and Y. Duan, *Chem. Rev.*, 2014, **114**, 6130-6178.
- 40 51. J. A. Hubbell and A. Chilkoti, *Science*, 2012, **337**, 303-305.
52. D. Jariwala, V. K. Sangwan, L. J. Lauhon, T. J. Marks and M. C. Hersam, *Chem. Soc. Rev.*, 2013, **42**, 2824-2860.
53. A. Biswas, I. S. Bayer, A. S. Biris, T. Wang, E. Dervishi and F. Faupel, *Adv. Colloid Interface Sci.*, 2012, **170**, 2-27.
- 45 54. H.-D. Yu, M. D. Regulacio, E. Ye and M.-Y. Han, *Chem. Soc. Rev.*, 2013, **42**, 6006-6018.
55. T. Rajagopalan, K. Venumadhav, G. Arkasubhra, C. Nripen, G. Keshab and G. Shubhra, *Rep. Prog. Phys.*, 2013, **76**, 066501.
56. Y. Xia, Y. Xiong, B. Lim and S. E. Skrabalak, *Angew. Chem. Int. Ed.*, 2009, **48**, 60-103.
57. N. P. E. Barry, A. Pitto-Barry, A. M. Sanchez, A. P. Dove, R. J. Procter, J. J. Soldevila-Barreda, N. Kirby, I. Hands-Portman, C. J. Smith, R. K. O'Reilly, R. Beanland and P. J. Sadler, *Nat. Commun.*, 2014, **5**, 3851.
- 50 58. N. P. E. Barry, A. Pitto-Barry, I. Romero-Canelon, J. Tran, J. J. Soldevila-Barreda, I. Hands-Portman, C. J. Smith, N. Kirby, A. P. Dove, R. K. O'Reilly and P. J. Sadler, *Faraday Discuss.*, 2014, **175**, 229-240.

Claims

1. A method of producing single metal atoms on a graphitic surface, the method comprising the steps of:
 - a. providing a metal complex;
 - 5 b. mixing the metal complex with a carbon-containing species to form an encapsulant comprising the metal complex encapsulated by the carbon-containing species;
 - c. depositing the encapsulant; and
 - 10 d. irradiating the deposited encapsulant to form a graphitic surface on which one or more isolated metal atoms of the metal complex are located.
2. A method according to Claim 1, comprising irradiating the mixture in an oxidising or non-oxidising environment.
- 15 3. A method according to Claim 1 or 2, comprising irradiating the deposited encapsulant, preferably with high energy radiation, for sufficient time to allow or cause plural isolated metal atoms to agglomerate on the surface.
- 20 4. A method according to any of Claims 1, 2 or 3, comprising irradiating the deposited encapsulant, preferably with high energy radiation, for sufficient time to allow or cause plural metal atoms to agglomerate on the surface to form clusters, and preferably for sufficient time to allow or cause metal atoms to agglomerate to form nanocrystals.
- 25 5. A method according to Claim 4, comprising irradiating the deposited encapsulant for up to 1hr thereby to produce nanocrystals typically of 0.5 to $60 \times 10^{-9}\text{m}$, and preferably from $1.5 - 50 \times 10^{-9}\text{m}$ in diameter.
- 30 6. A method according to any preceding Claim, comprising providing plural metal complexes each based on a different metal and mixing at least one of the complexes in the, or each in a respective carbon-containing species to form plural encapsulants.
- 35 7. A method according to Claim 6, comprising selecting a molar ratio of the plural metals in the plural metal complexes and irradiating, the deposited encapsulants to generate a heterometal nanocrystal with a mixing ratio preferably or substantially the same as the molar ratio.
- 40 8. A method according to any preceding Claim, wherein step a comprises providing a metal complex in which the metal is selected from molybdenum, tungsten, tin, lead, arsenic, antimony, and bismuth, indium, gallium, osmium, ruthenium, rhodium, platinum, palladium, iridium, gold, silver, cobalt, iron, nickel, chromium, manganese, vanadium, lanthanides, e.g. Ru^{II} or Os^{II} ,

9. A method according to any preceding Claim wherein the ligands of the metal complex are selected from an arene and/or cyclopentadienyl derivative, and/or a carborane.
10. A method according to any preceding Claim, comprising providing as at least a component of a ligand of the metal complex, a species able to dope the graphitic structure upon exposure to the heat energy, preferably high energy radiation.
11. A method according to any preceding Claim, wherein at least one of the ligands comprises a chalcogen (for example one or more of sulphur, selenium, tellurium, oxygen) or a halogen (for example one of iodine, bromine) or a pnictogen (for example one of nitrogen, phosphorous, arsenic, antimony) and wherein, upon irradiation in step d said chalcogen, halogen or pnictogen dopes the graphitic structure.
12. A method according to Claim 11, wherein at least one of the ligands comprises a dithio-carborane or diselenate-carborane and wherein, upon irradiation in step d said boron, sulphur or selenium dopes the graphitic structure.
13. A method according to any preceding Claim, wherein step b comprises mixing the metal complex with a polymer, typically in a solvent or a mixture of solvents, for example tetrahydrofuran/water (1:10 v/v) to form a solution.
14. A method according to Claim 13, wherein the polymer is a di or tri-block copolymer.
15. A method according to any preceding Claim, wherein said mixing of step b causes the carbon-containing species or polymer to form one or more of vesicles, lipid bilayer, micelles, nanocapsules, nanoparticles, metal organic frameworks (MOF), thereby to form the soluble encapsulant and to encapsulate the metal complex, preferably said mixing causes said carbon-containing species or polymer to form micelles, thereby to encapsulate the metal complex.
16. A method according to any preceding Claim, wherein step d is conducted by irradiating with high energy radiation, typically greater than 1 pA cm^{-2}
17. A method according to any preceding Claim, wherein step d is practiced by use of one or more of an electron beam, a laser beam, UV light, plasma, infra-red radiation, microwaves, γ -rays.
18. A method of forming metal nanocrystals, the method comprising exposing a metal complex encapsulated in a soluble, carbon-containing matrix to heat energy, preferably high energy radiation, to form a graphitic substrate and allowing or causing metal atoms to agglomerate on the graphitic substrate to form nanocrystals and harvesting the nanocrystals.
19. A method according to Claim 18, wherein harvesting comprises dissolving or otherwise removing the graphitic substrate on which the nanocrystals are located.

20. A method according to any preceding Claim, wherein the graphitic substrate is graphene, or graphene-like which is formed from the carbon-containing species or carbon-containing matrix and removing the substrate comprises dissolving the graphene.
21. A method according to any of Claims 17, 18 or 19, comprising forming a micelle containing the complex, thereby suspending the complex in the carbon-containing matrix.
22. A method according to any preceding Claim, comprising using a laser beam, electron beam or microwaves to irradiate the fluid, carbon-containing matrix and selecting a particular intensity, energy and/or irradiation time to agglomerate atoms, for example to grow nanocrystals, of a desired size and/or at a specific location.
23. A method of forming graphene, the method comprising irradiating micelles, lipids, vesicles or other carbon-containing species with high energy radiation.
24. A method of agglomerating metal atoms, the method comprising providing plural individual metal atoms on a graphitic surface, preferably comprised of one or more layers of graphene, and irradiating the surface to allow or cause the metal atoms to agglomerate.
25. A method according to Claim 24, comprising irradiating the surface for sufficient time to allow or cause atoms to agglomerate to form nanoalloys or nanocrystals.
26. A method according to Claim 24 or 25, wherein the irradiation is provided by a beam of high energy radiation, for example an electron beam, laser beam, focused UV light or IR radiation, microwaves, x-rays.
27. A solvent-soluble micelle comprising a polymeric shell containing a substantially solvent-insoluble metal complex, the or at least one of the ligands comprising one or more of boron, phosphorus, nitrogen, sulfur, selenium, tellurium and the metal being selected from molybdenum, tungsten, tin, lead, arsenic, antimony, and bismuth, indium, gallium, osmium, ruthenium, rhodium, platinum, palladium, iridium, gold, silver, cobalt, iron, nickel, chromium, manganese, vanadium, lanthanides.
28. A micelle according to Claim 27, wherein the metal of the metal complex is selected from indium, gallium, ruthenium and/or osmium, e.g. Ru^{II} or Os^{II},
29. A micelle according to Claim 27 or 28, wherein the ligands comprise one or more of an arene or cyclopentadienyl derivative, together with one or more, other ligand, e.g. a dithio-carborane or diselenate-carborane.

30. A micelle according to Claim 27, 28 or 29, further comprising a second solvent insoluble metal complex, wherein the second metal is different from the first.

5 31. A micelle according to Claim 30, wherein the second metal is selected from molybdenum, tungsten, tin, lead, arsenic, antimony, and bismuth, indium, gallium, osmium, ruthenium, rhodium, platinum, palladium, iridium, gold, silver, cobalt, iron, nickel, chromium, manganese, vanadium, lanthanides.

10 32. A micelle according to any of Claims 27 to 31, wherein the micelle is formed from di-block or tri-block copolymers.

33. A micelle according to any of Claims 27 to 32, wherein the micelle is formed from P123 or other Pluronic® block copolymer.

15 34. A self-supporting graphitic structure comprising one or more dopants and one or more individual metal atoms movably located on the surface of the structure.

20 35. A graphitic structure according to Claim 34, wherein the dopant is selected from boron, phosphorus, nitrogen, sulfur, selenium, tellurium.

25 36. A graphitic structure according to Claim 34 or 35, wherein the metal is selected from one or more of molybdenum, tungsten, tin, lead, arsenic, antimony, and bismuth, indium, gallium, osmium, ruthenium, rhodium, platinum, palladium, iridium, gold, silver, cobalt, iron, nickel, chromium, manganese, vanadium, lanthanides.

37. A graphitic structure according to Claim 34, 35 or 36, further comprising at least one other, different metal.

30 38. A graphitic structure according to any of Claims 34 to 37, wherein the second metal is selected from molybdenum, tungsten, tin, lead, arsenic, antimony, and bismuth, indium, gallium, osmium, ruthenium, rhodium, platinum, palladium, iridium, gold, silver, cobalt, iron, nickel, chromium, manganese, vanadium, lanthanides.

35 39. A three dimensional nanocrystal comprising plural metal atoms, for example selected from molybdenum, tungsten, tin, lead, arsenic, antimony, and bismuth, indium, gallium, osmium, ruthenium, rhodium, platinum, palladium, iridium, gold, silver, cobalt, iron, nickel, chromium, manganese, vanadium, lanthanides.

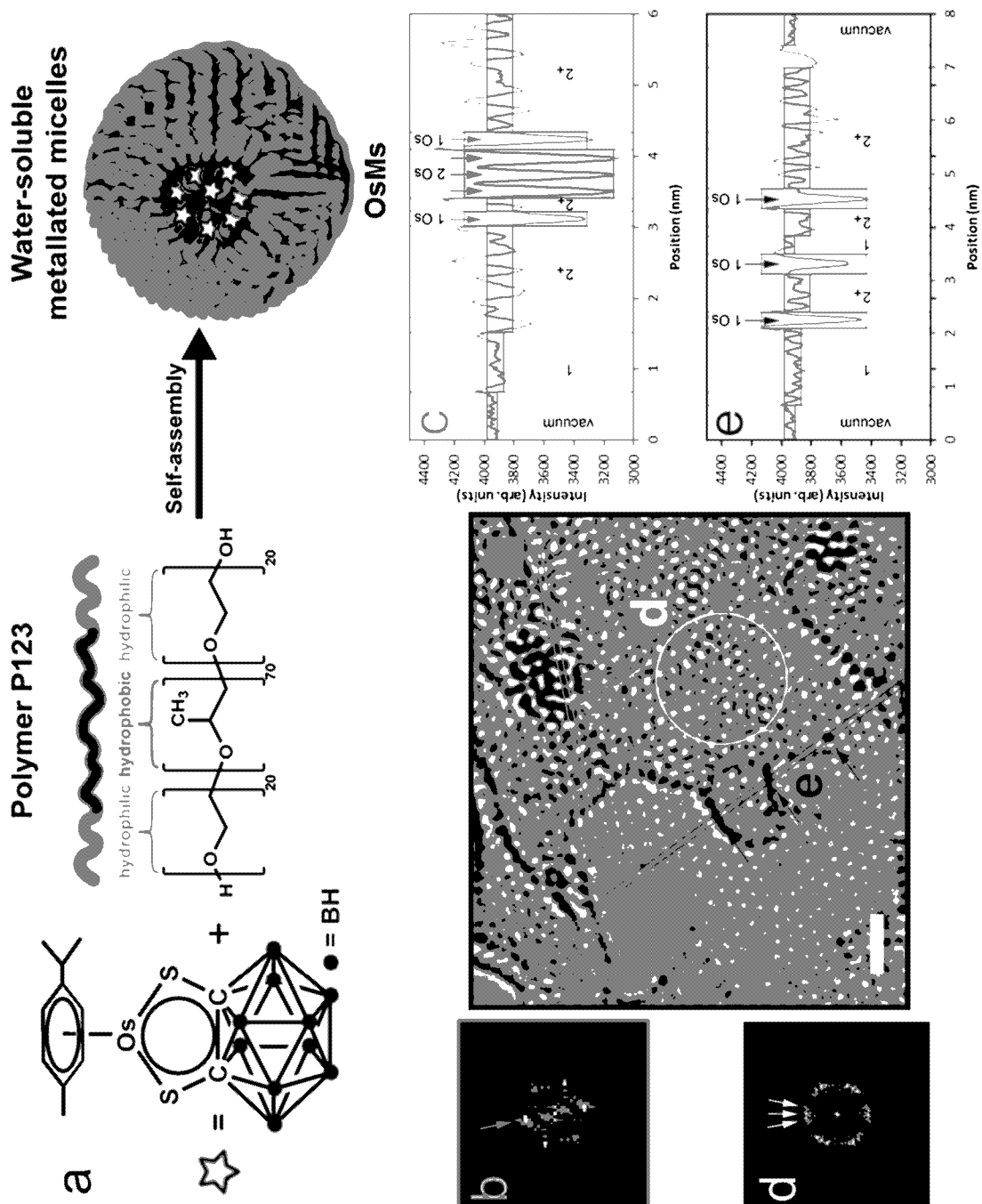


Figure 1

2/24

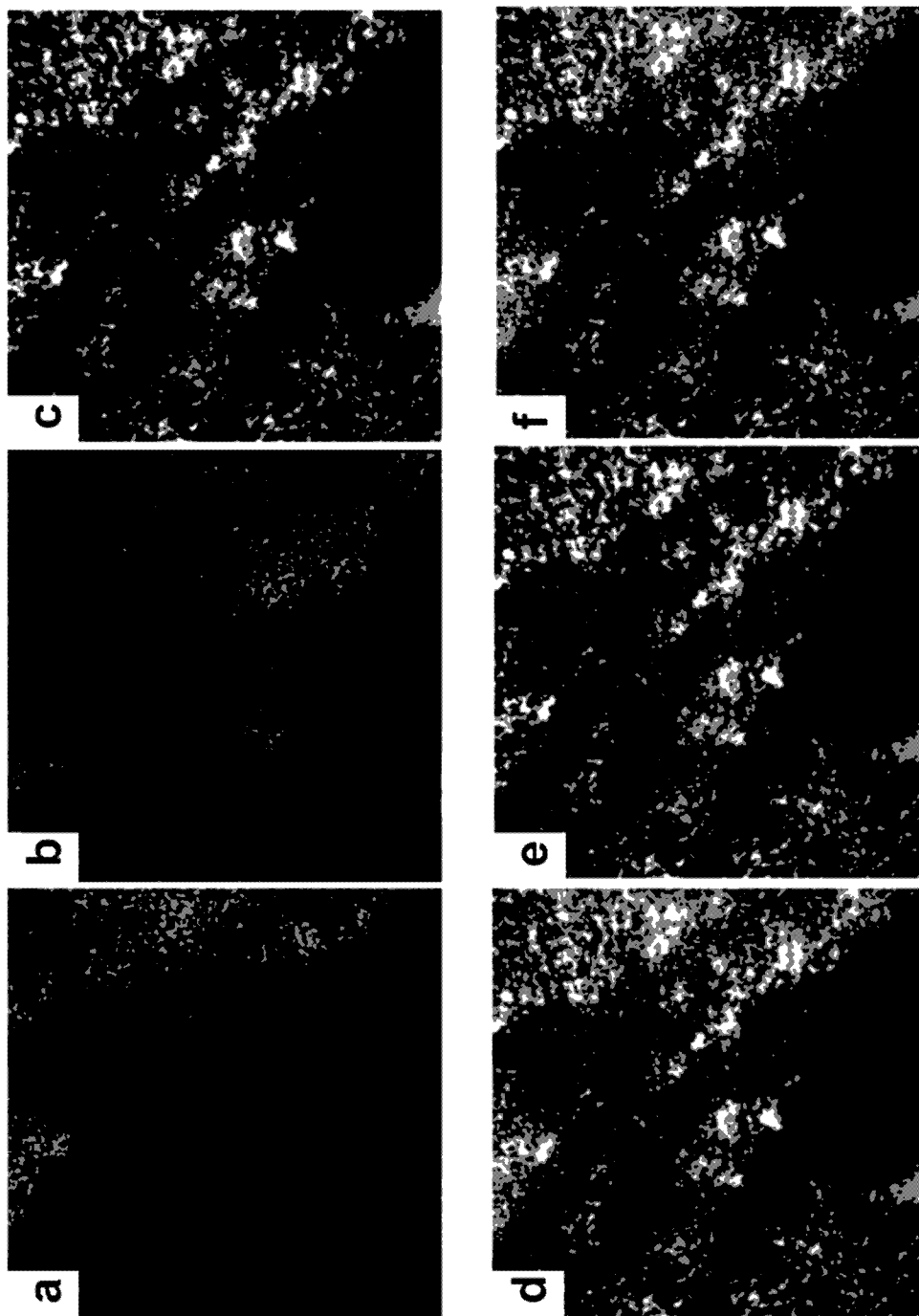
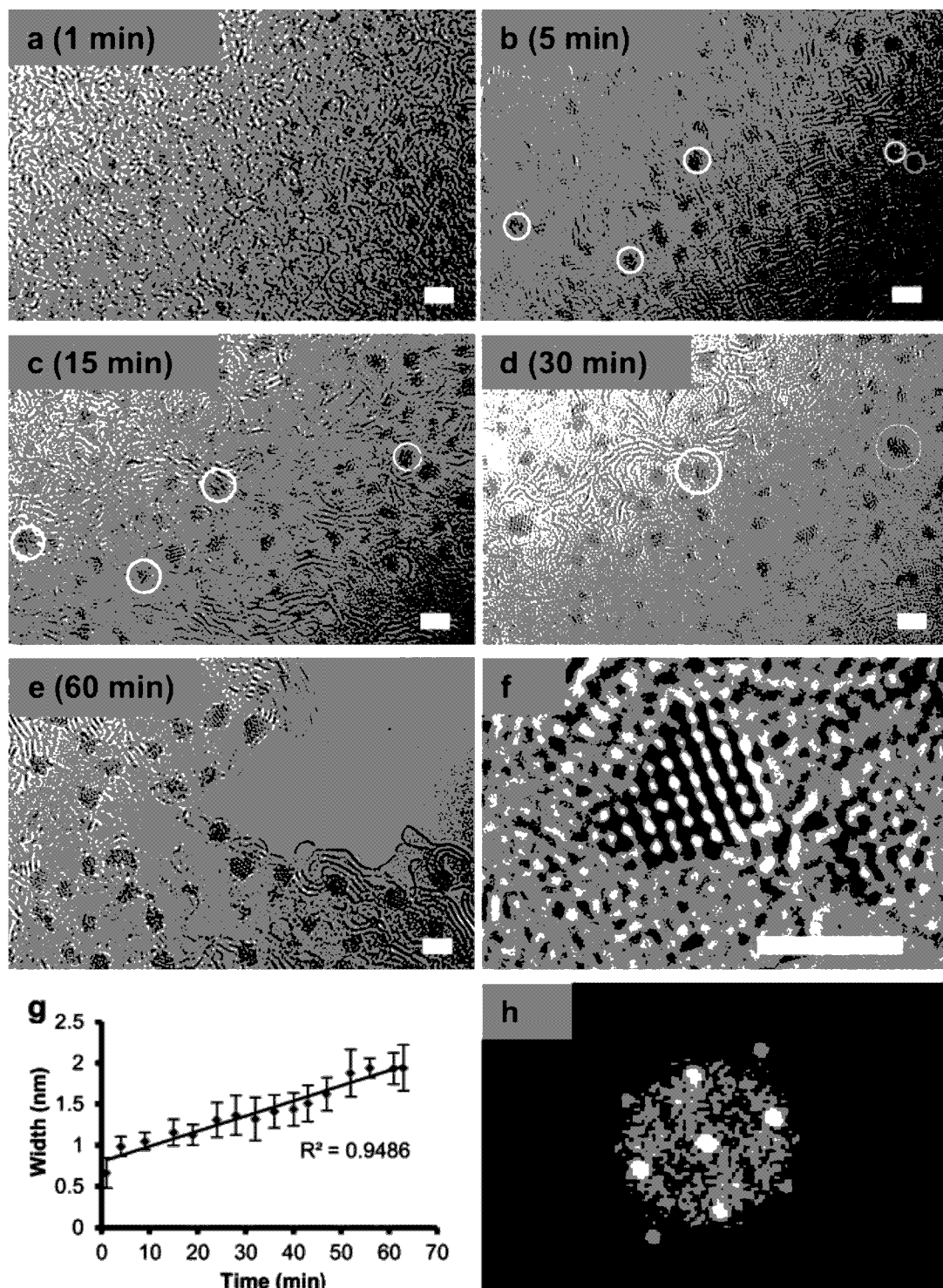
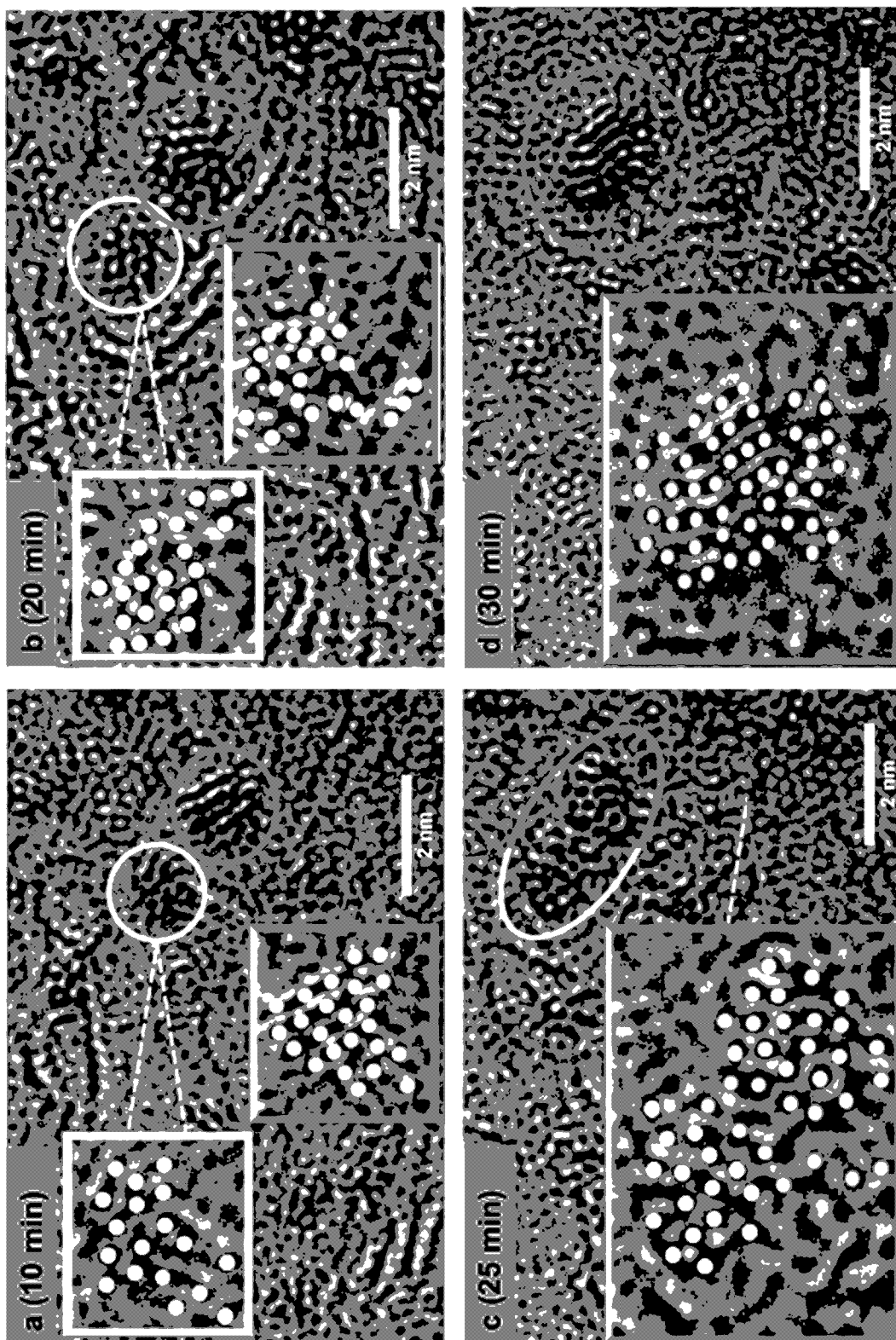


Figure 2

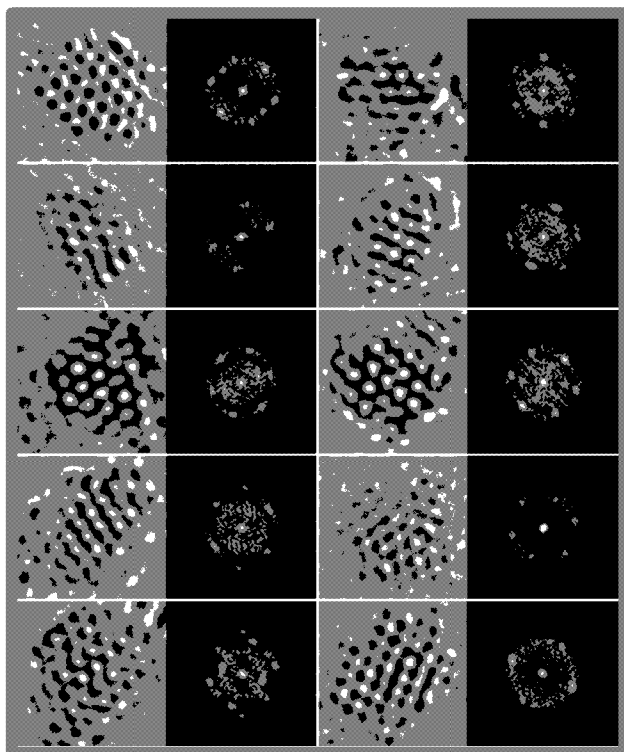
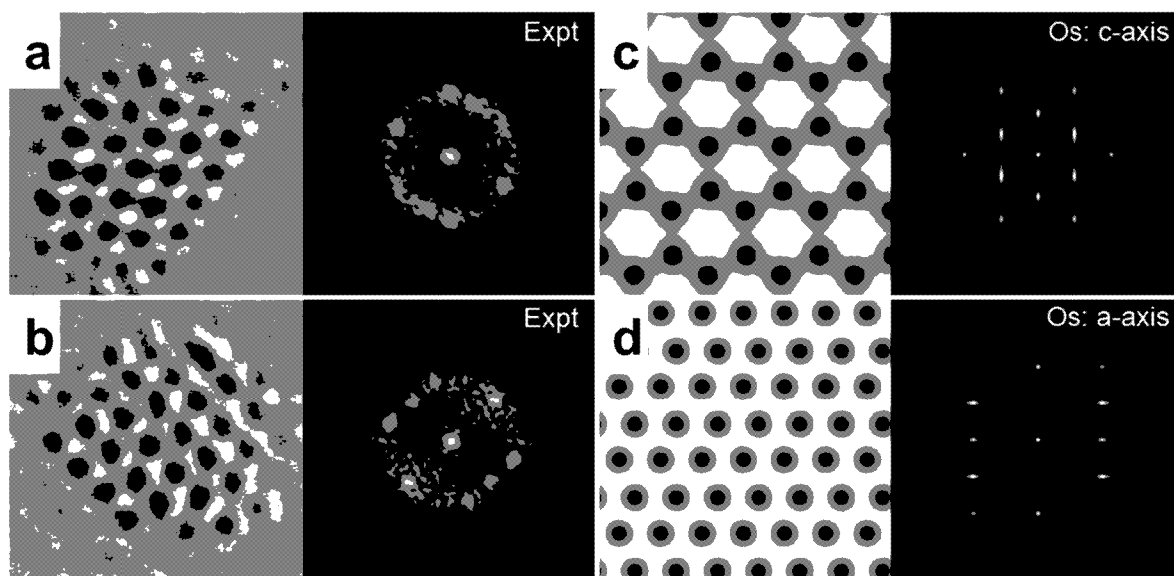
3/24

**Figure 3**

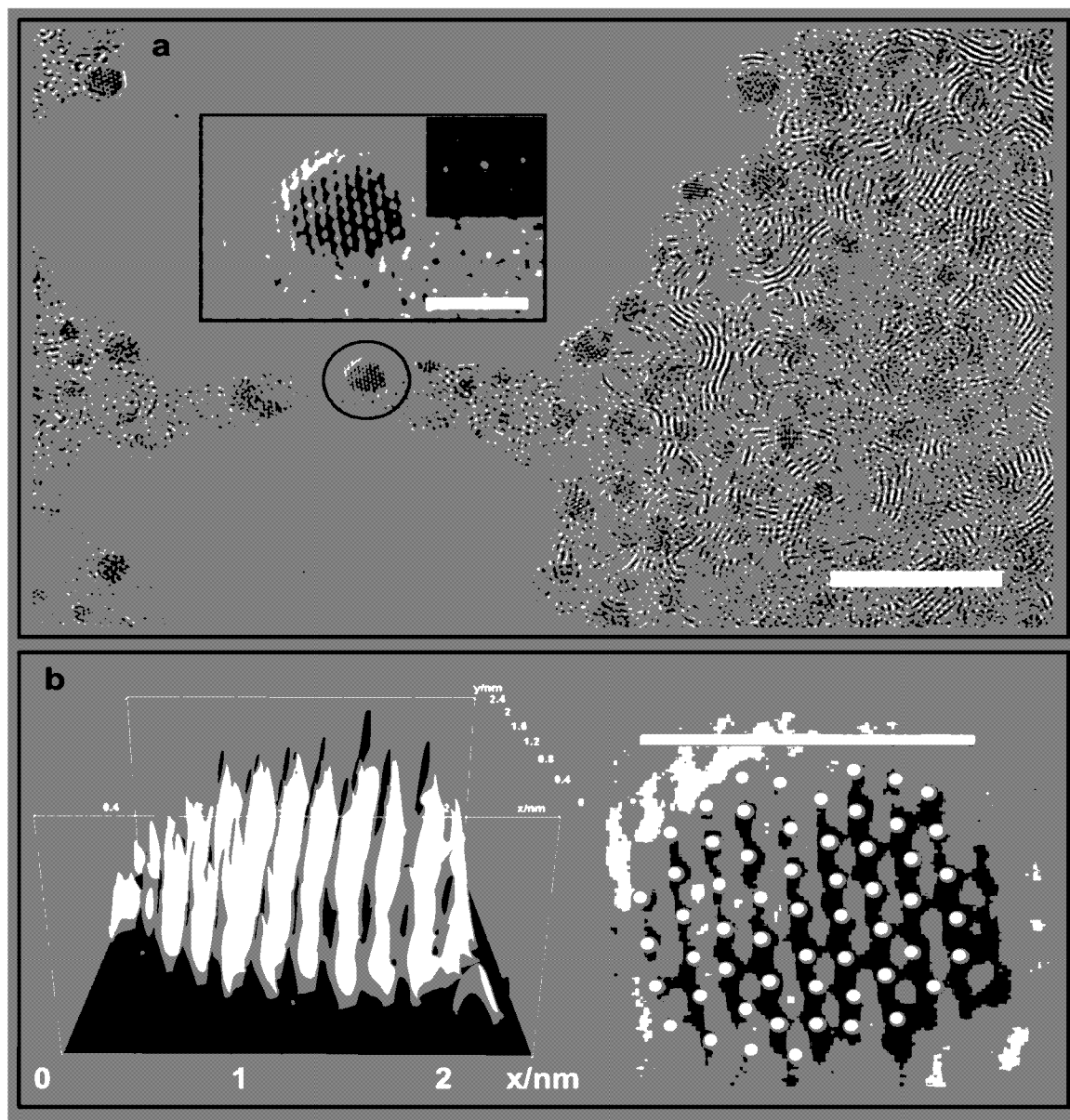
4/24

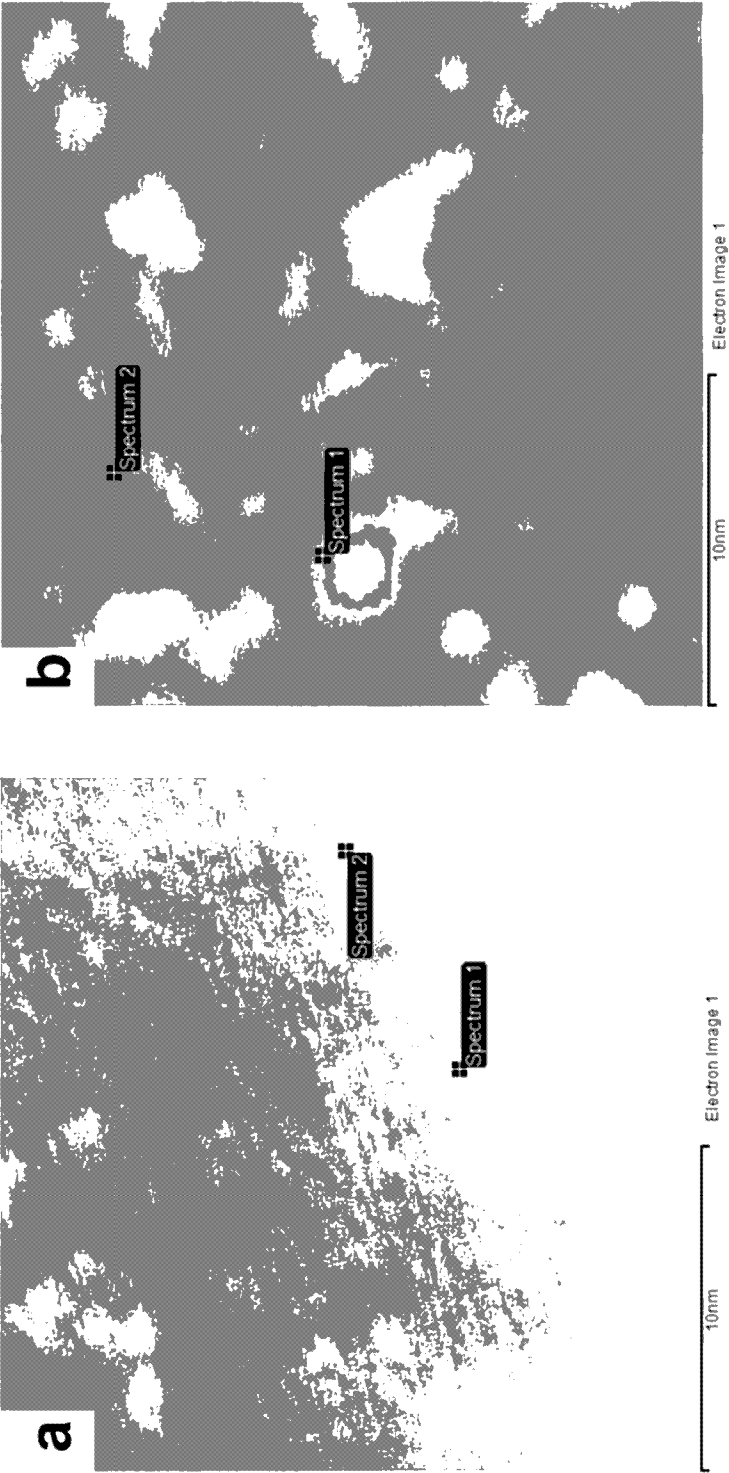
**Figure 4**

5/24

**Figure 5****Figure 6**

6/24

**Figure 7**



Spectrum	C (weight%)	O (weight%)	S (weight%)	Cu (weight%)	Ru (weight%)	Os (weight%)	Ru/Os (molar ratio)
(a)-1	49.22	5.72	1.11	30.23	5.00	8.30	1.13
(a)-2	44.20	9.46	1.08	34.19	3.87	7.21	1.01
(b)-1	32.41	10.51	0.70	38.39	5.98	12.00	0.94
(b)-2	45.58	10.95	1.10	34.42	2.53	5.42	0.88

Figure 8

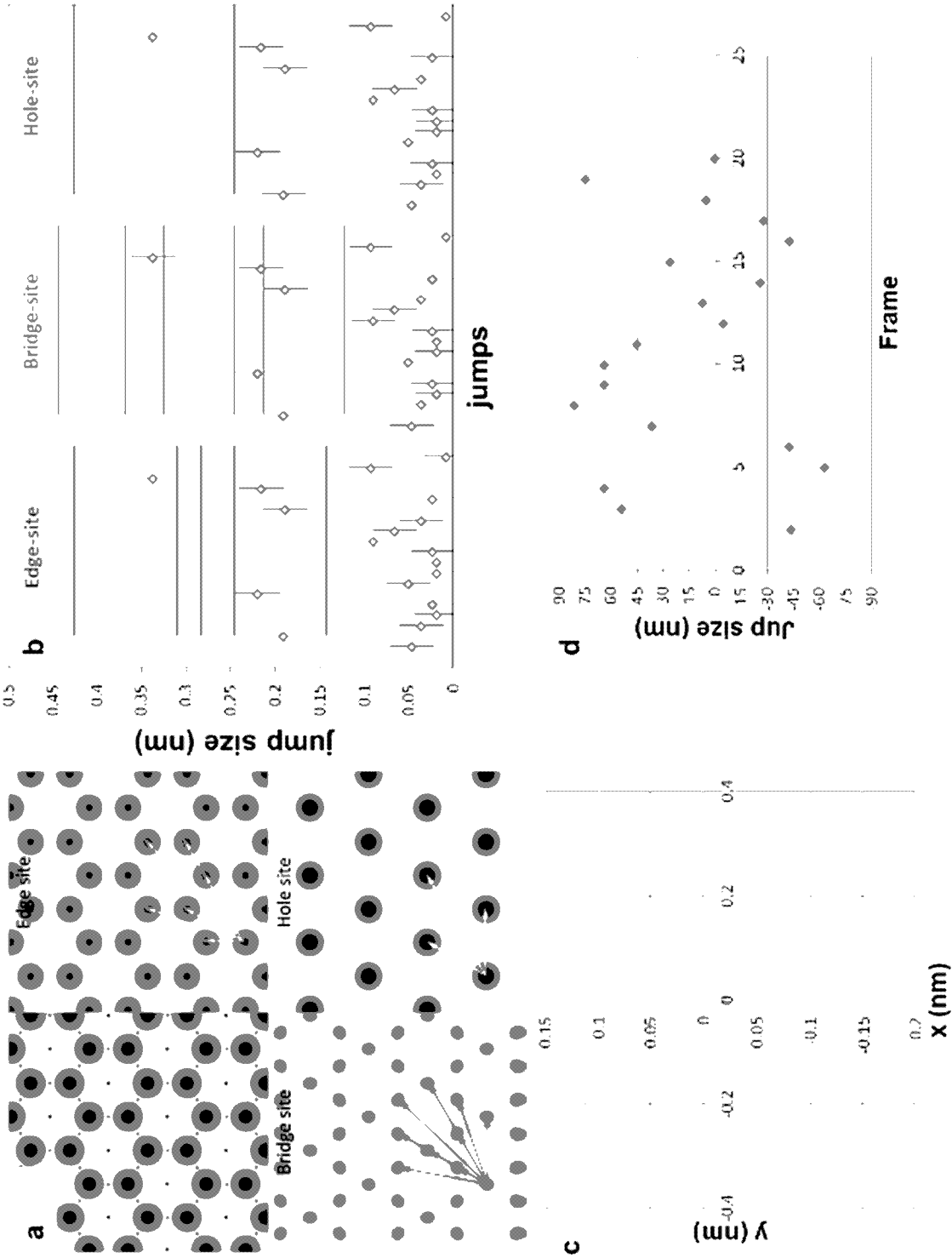


Figure 9

9/24

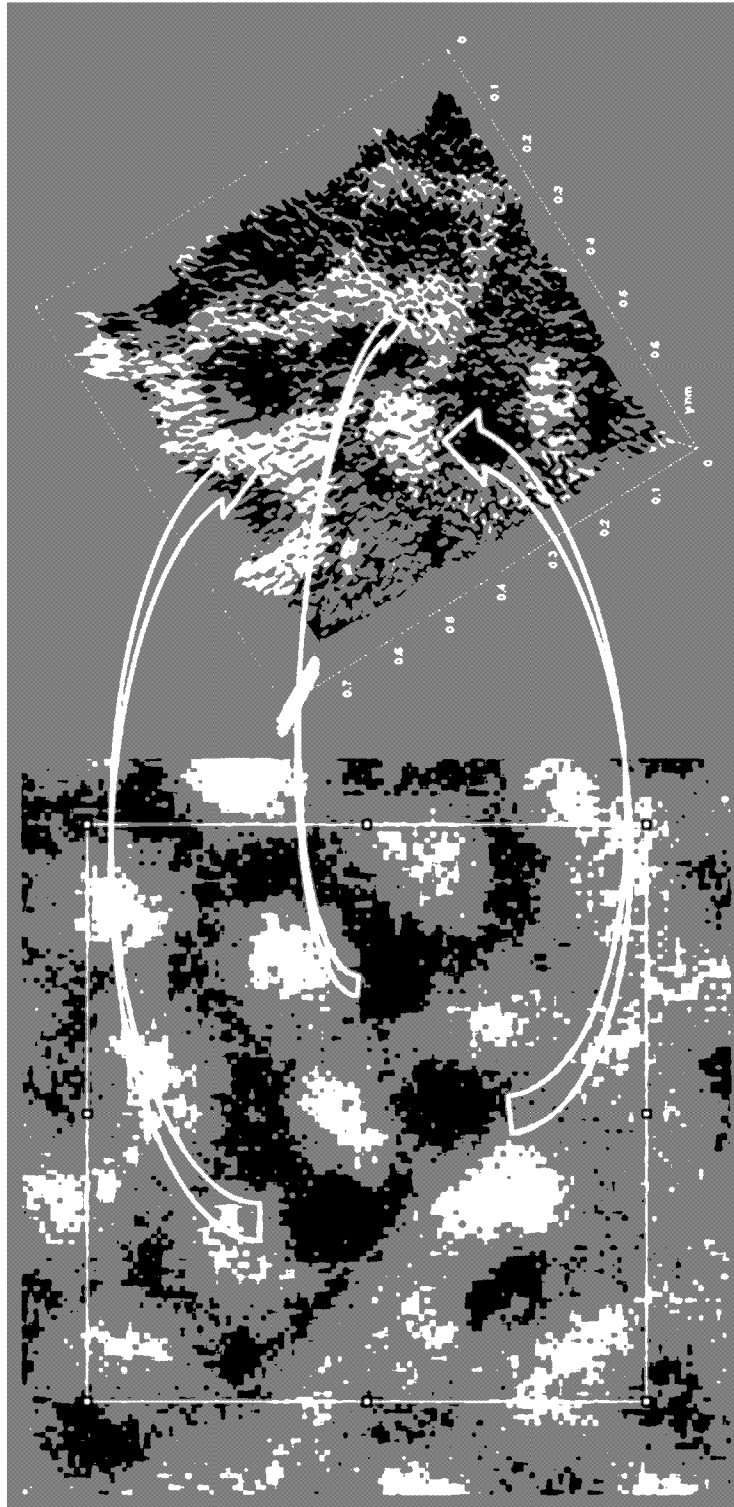


Figure 10

10/24

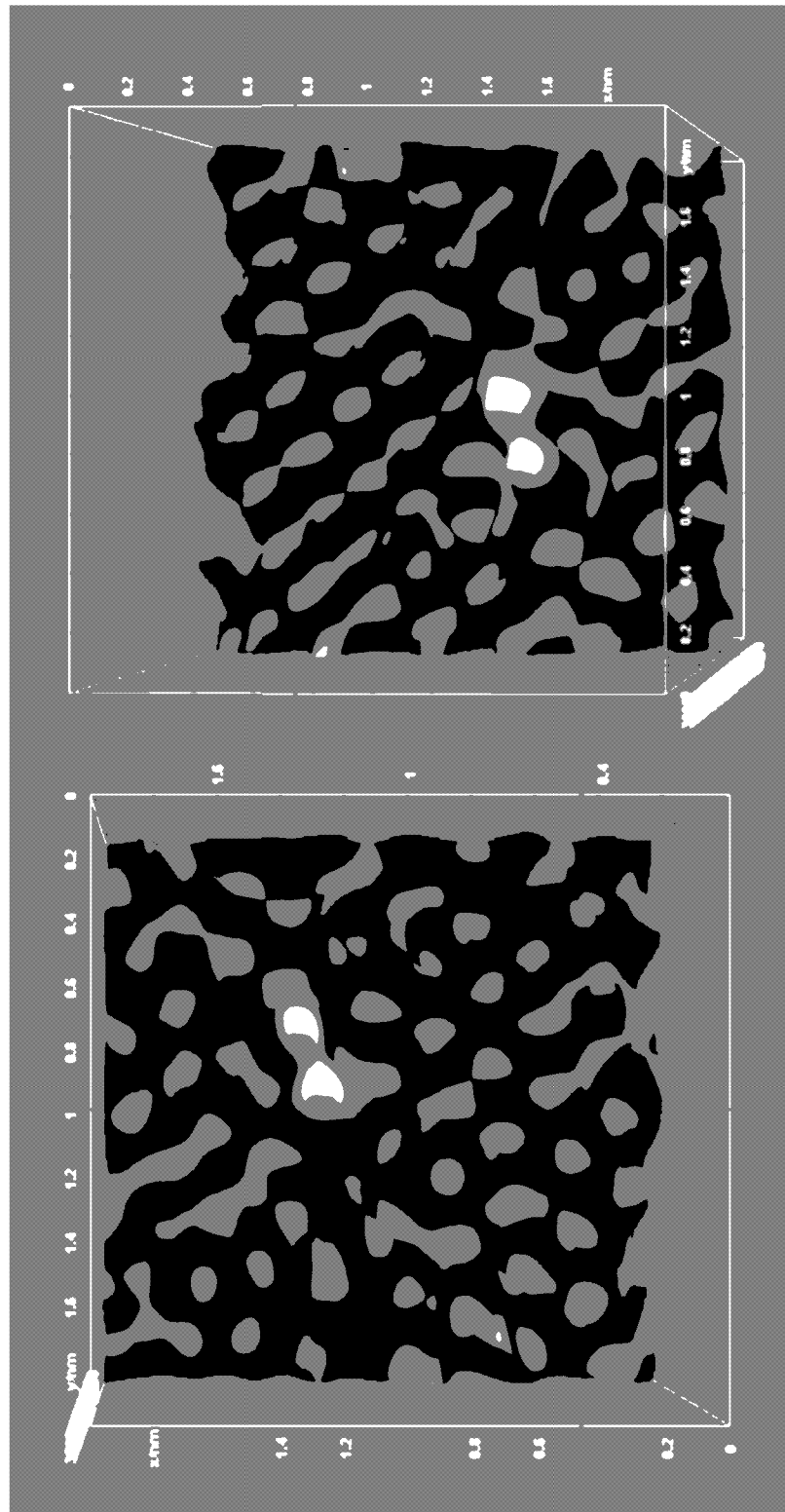
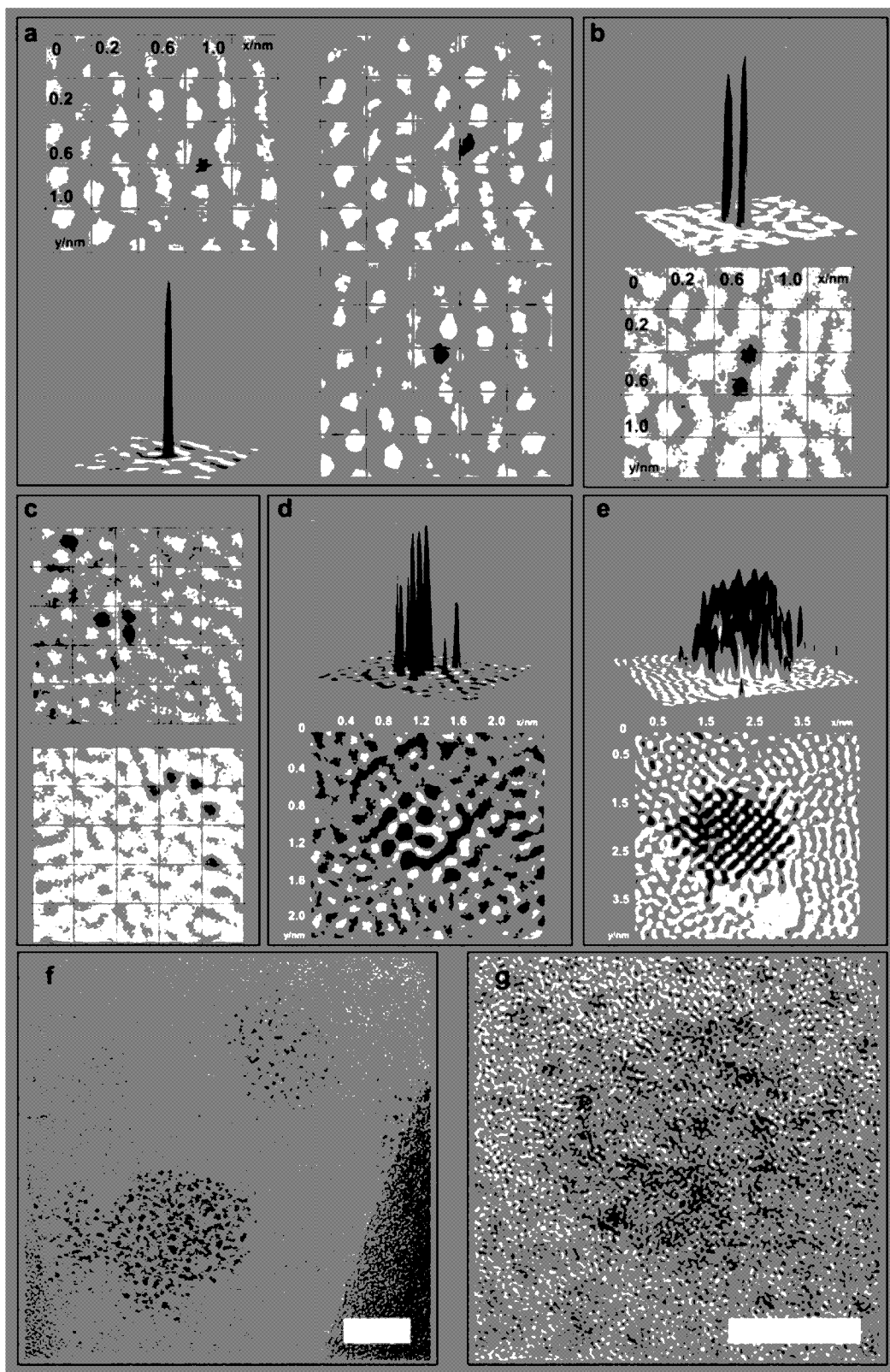
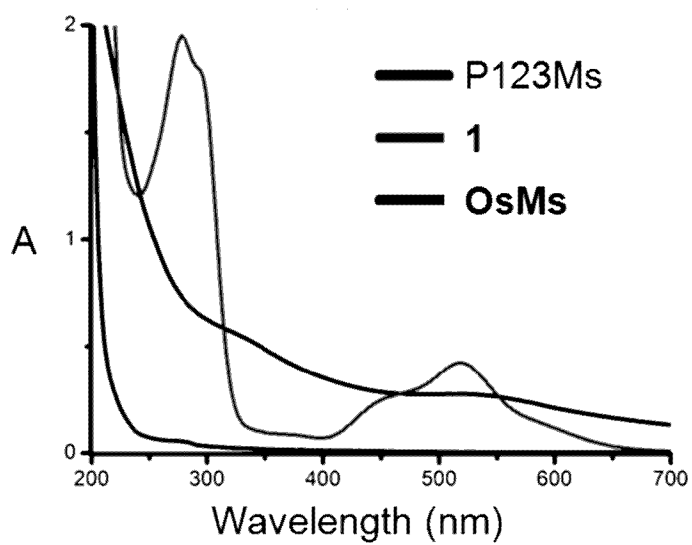


Figure 11

11/24

**Figure 12**

12/24

**Figure 13**

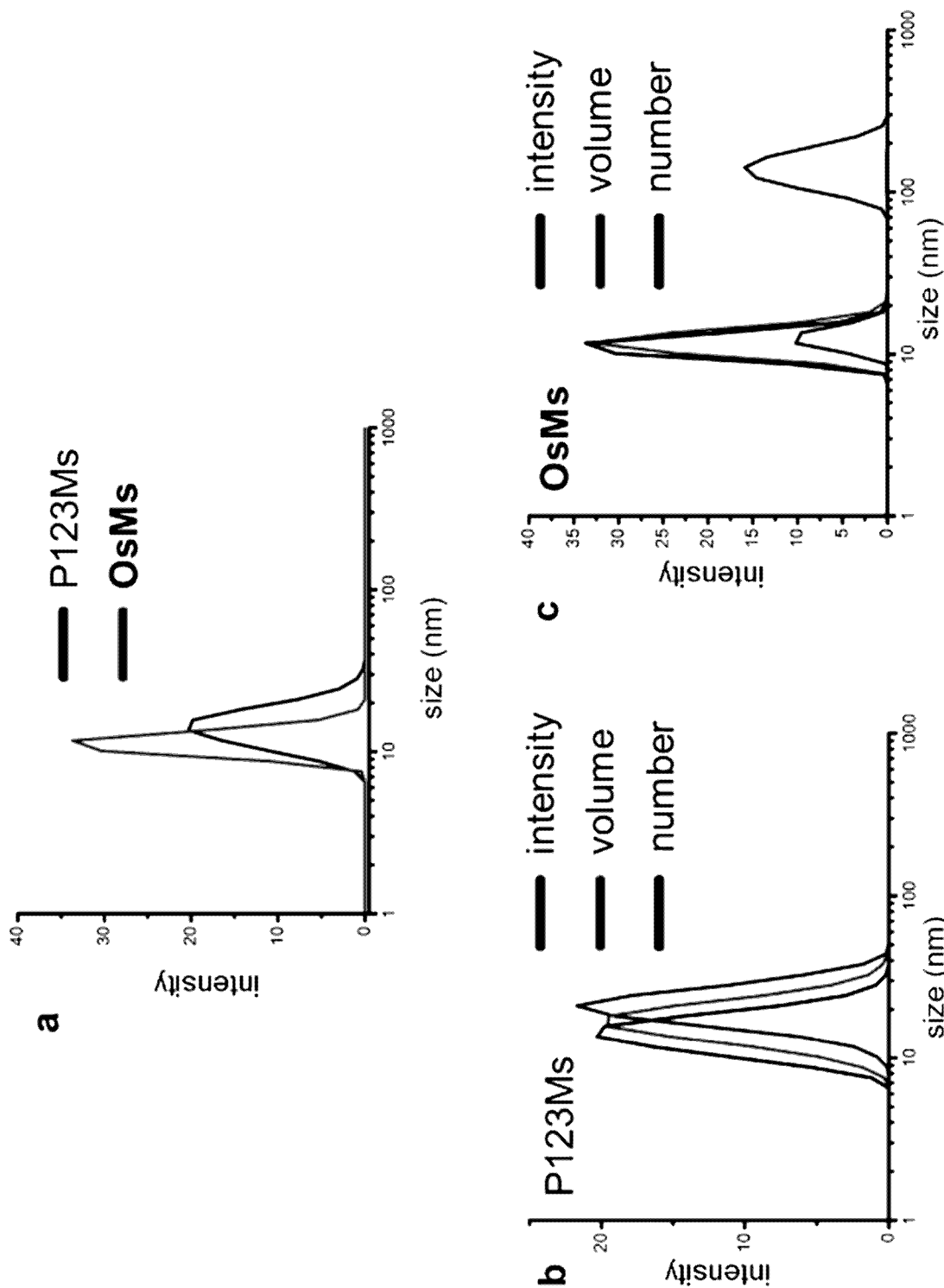


Figure 14

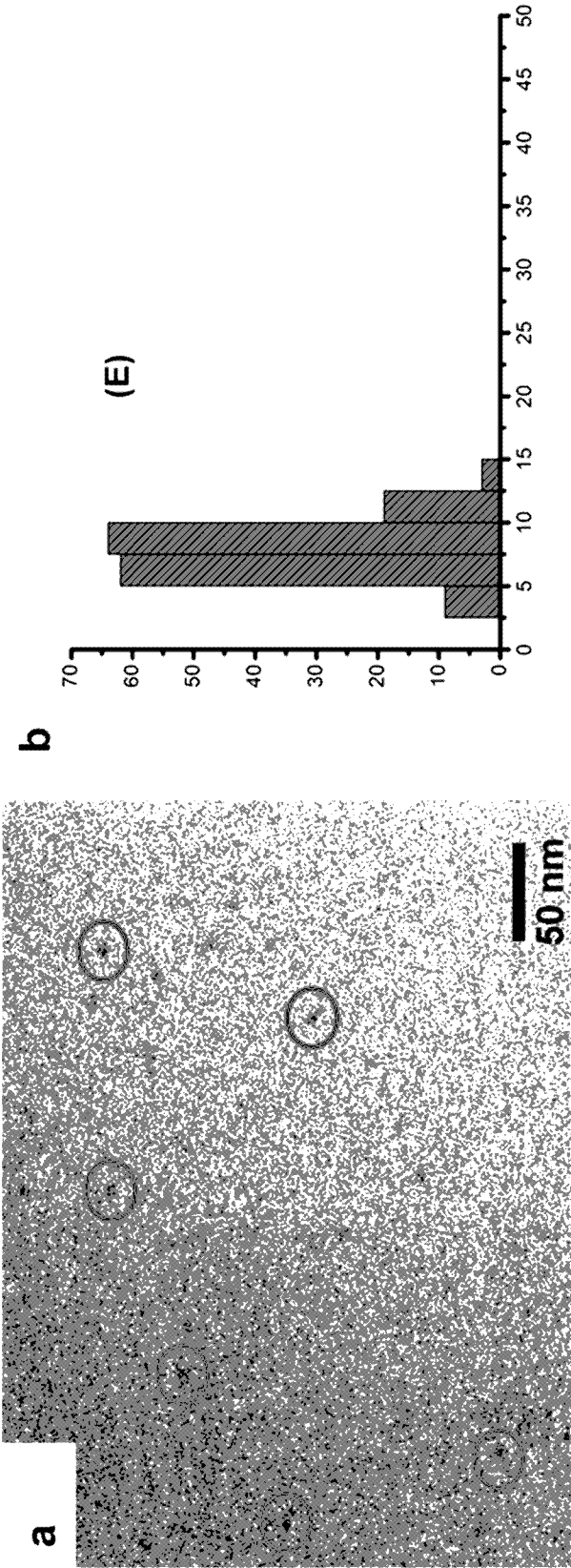


Figure 15

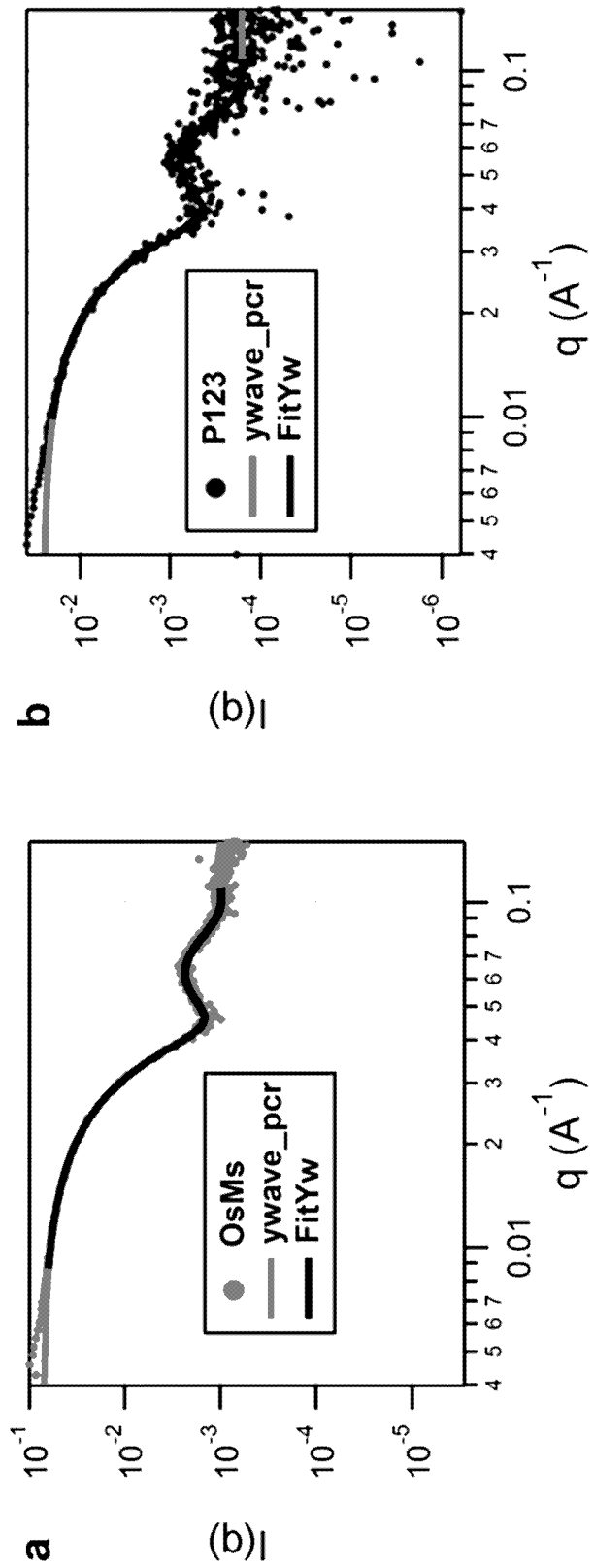


Figure 16

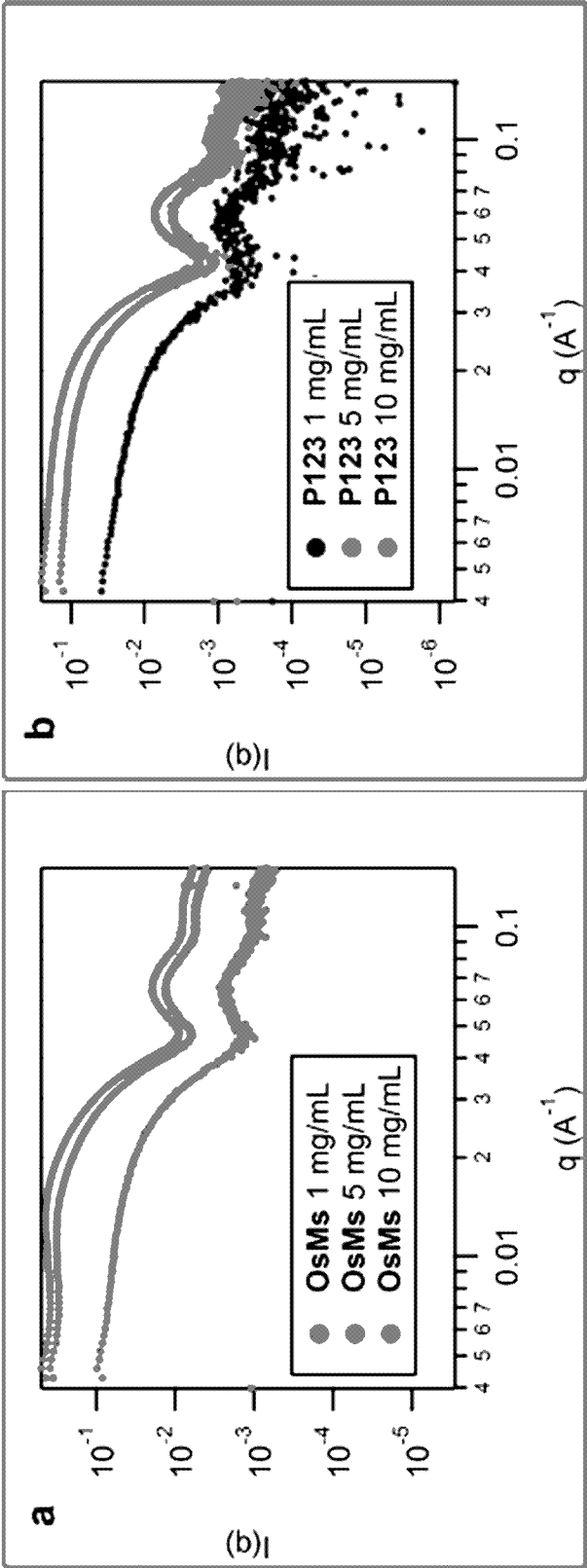
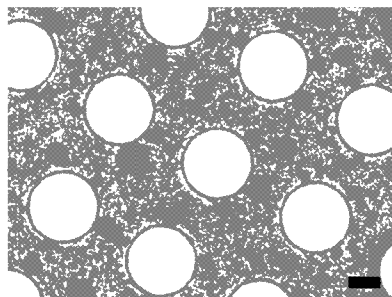
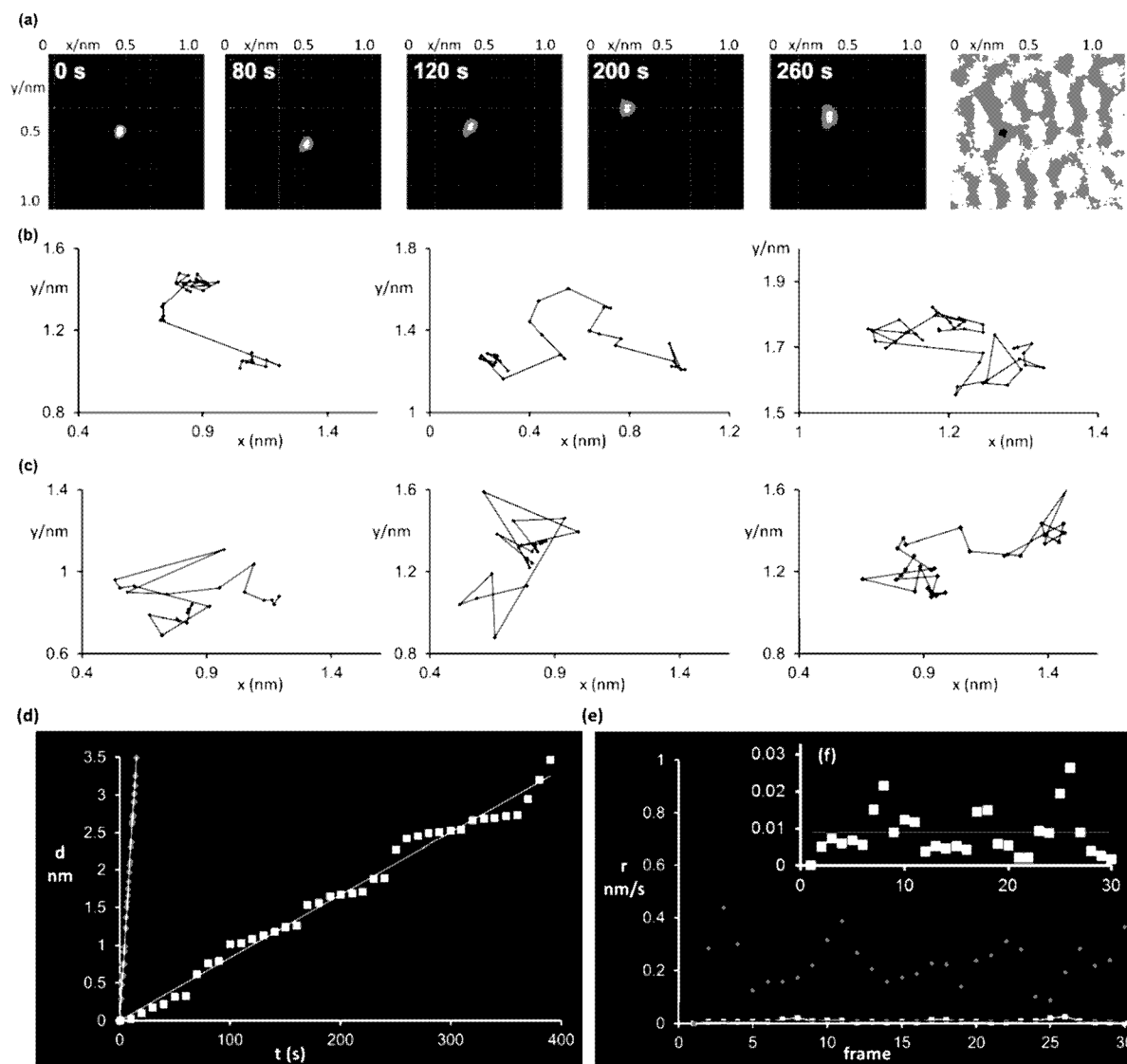
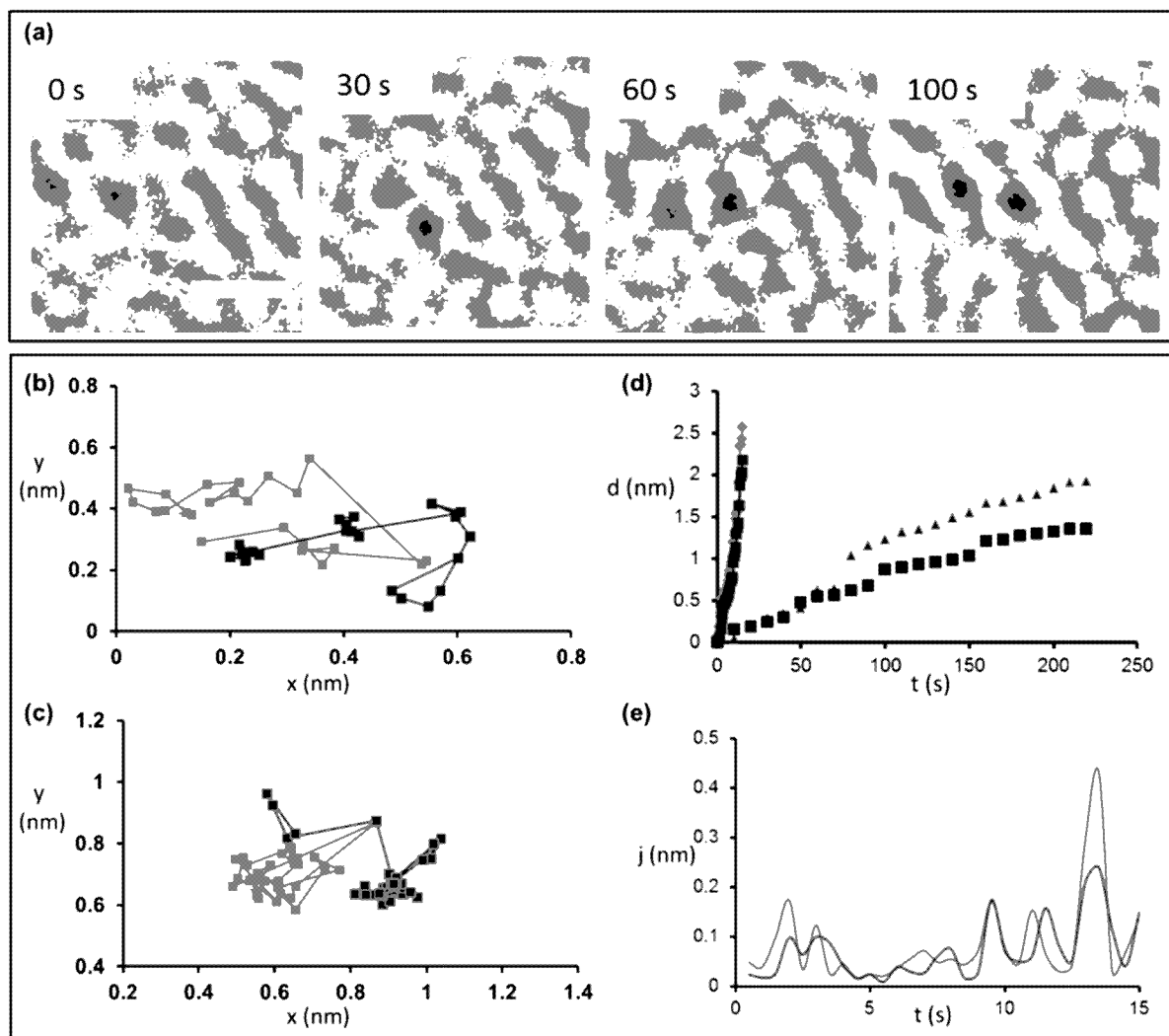


Figure 17

17/24

**Figure 18****Figure 19**

18/24

**Figure 20**

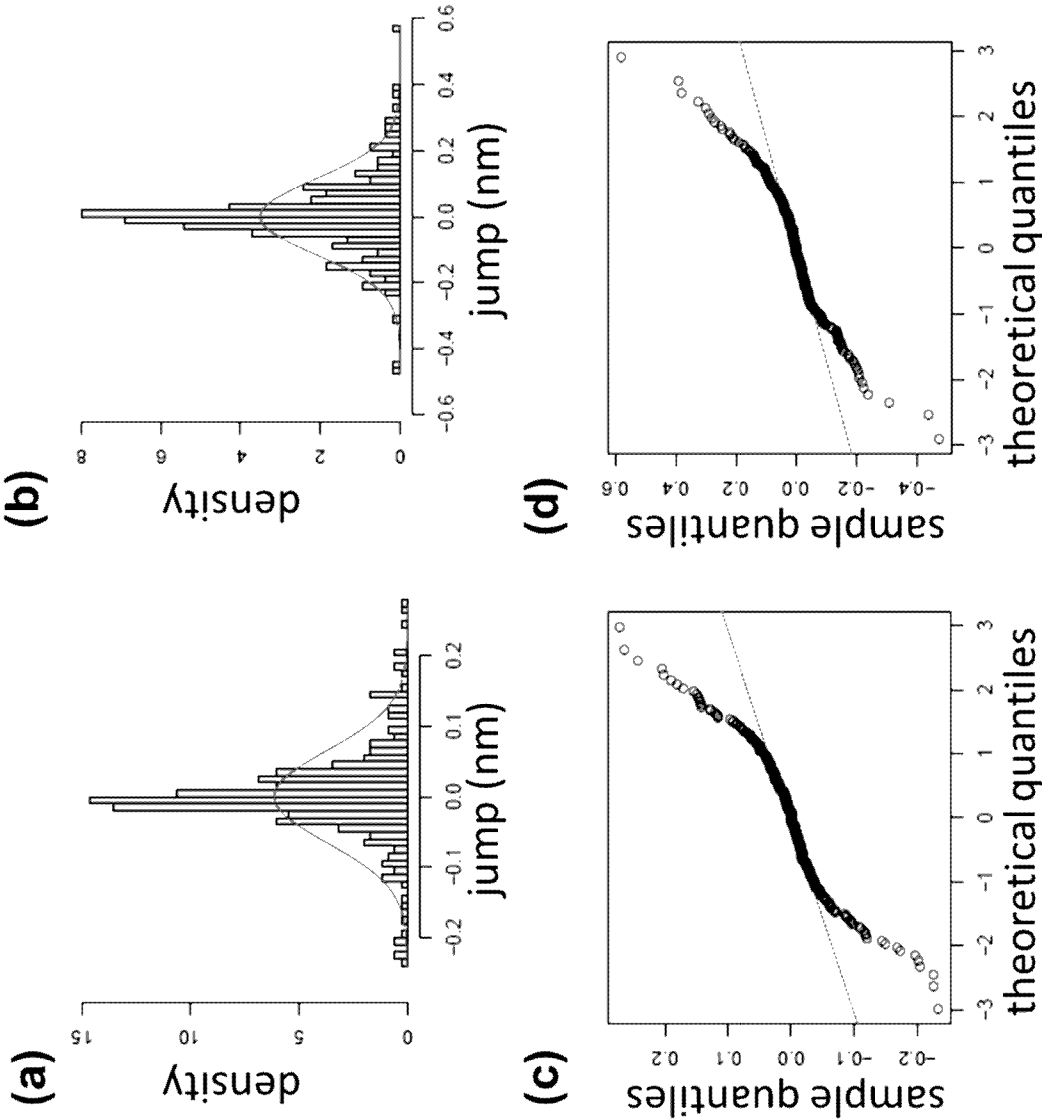


Figure 21

20/24

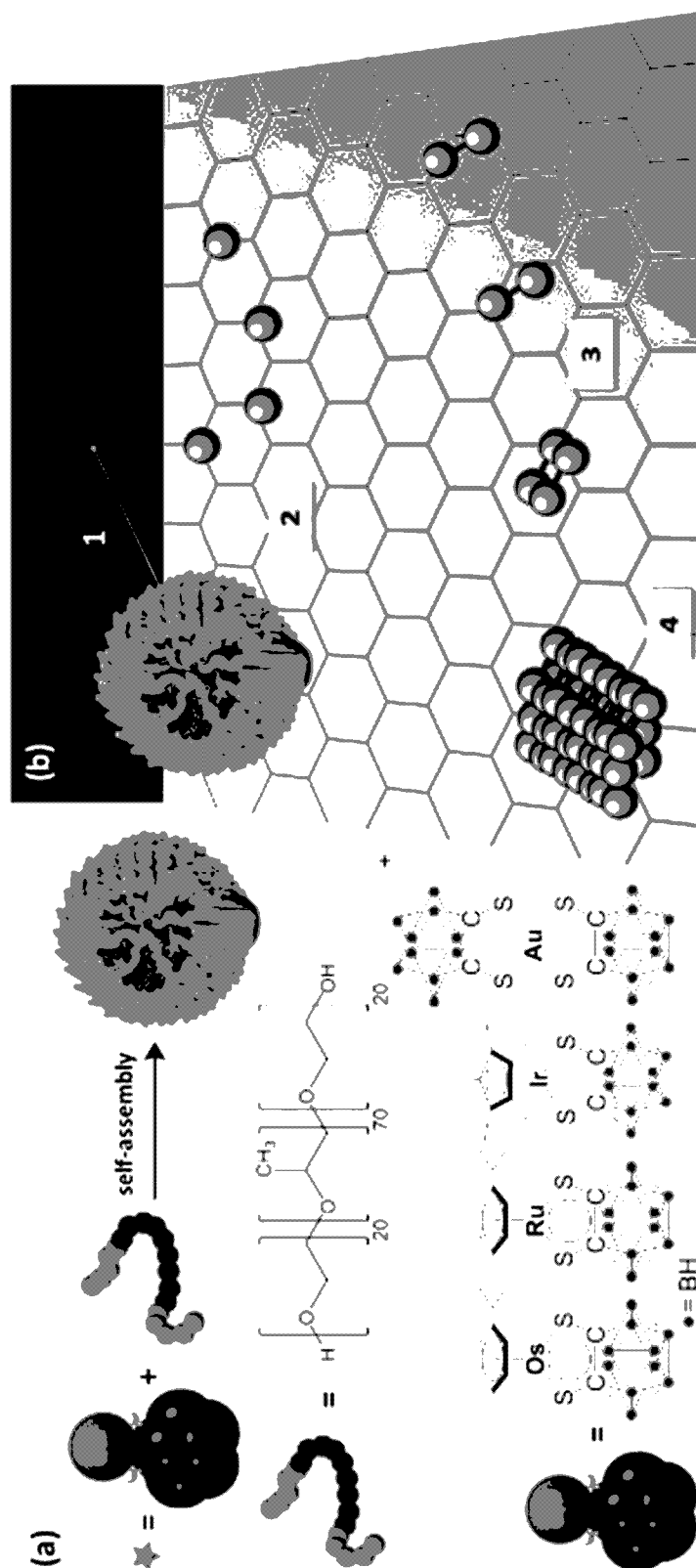
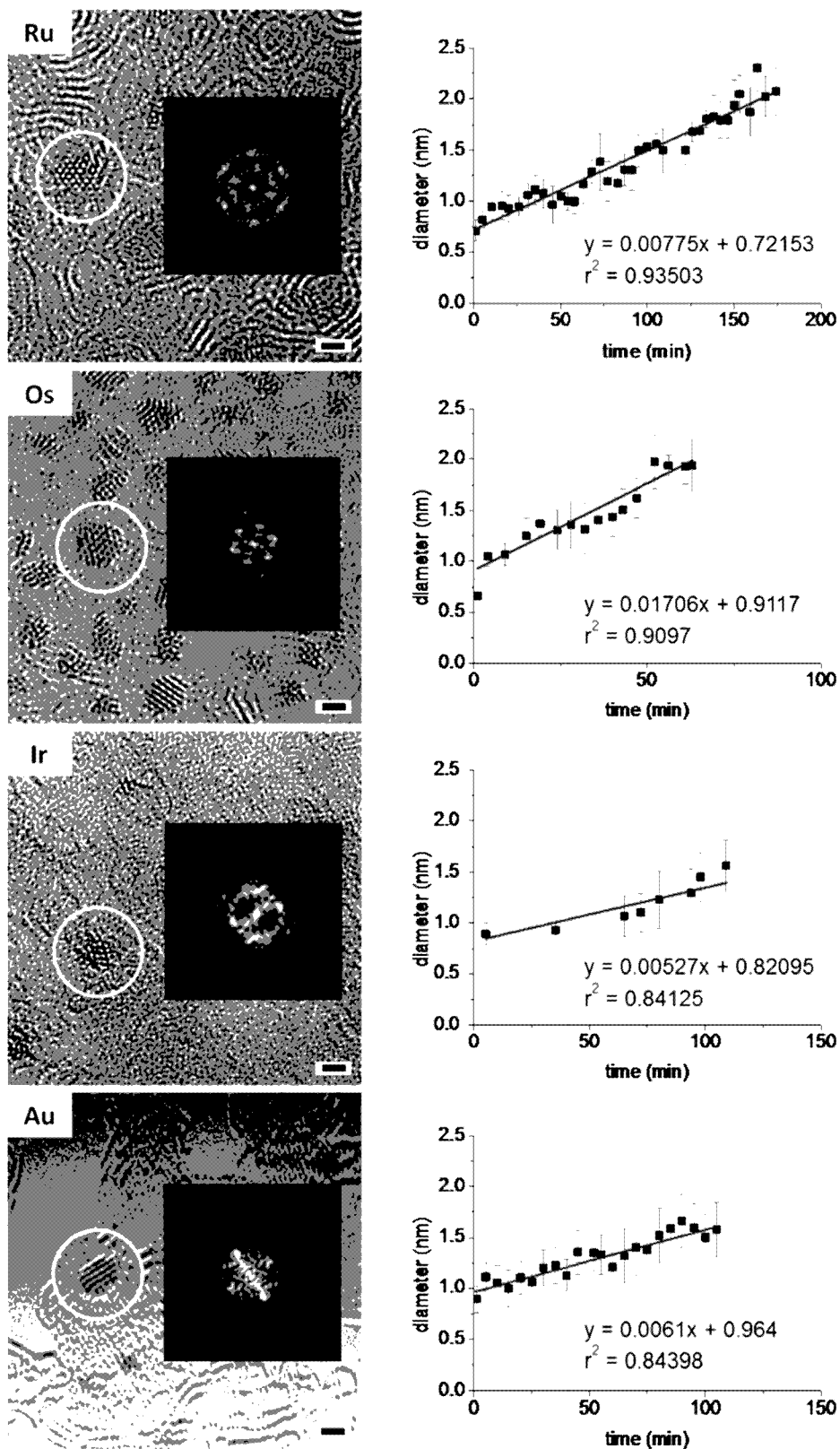
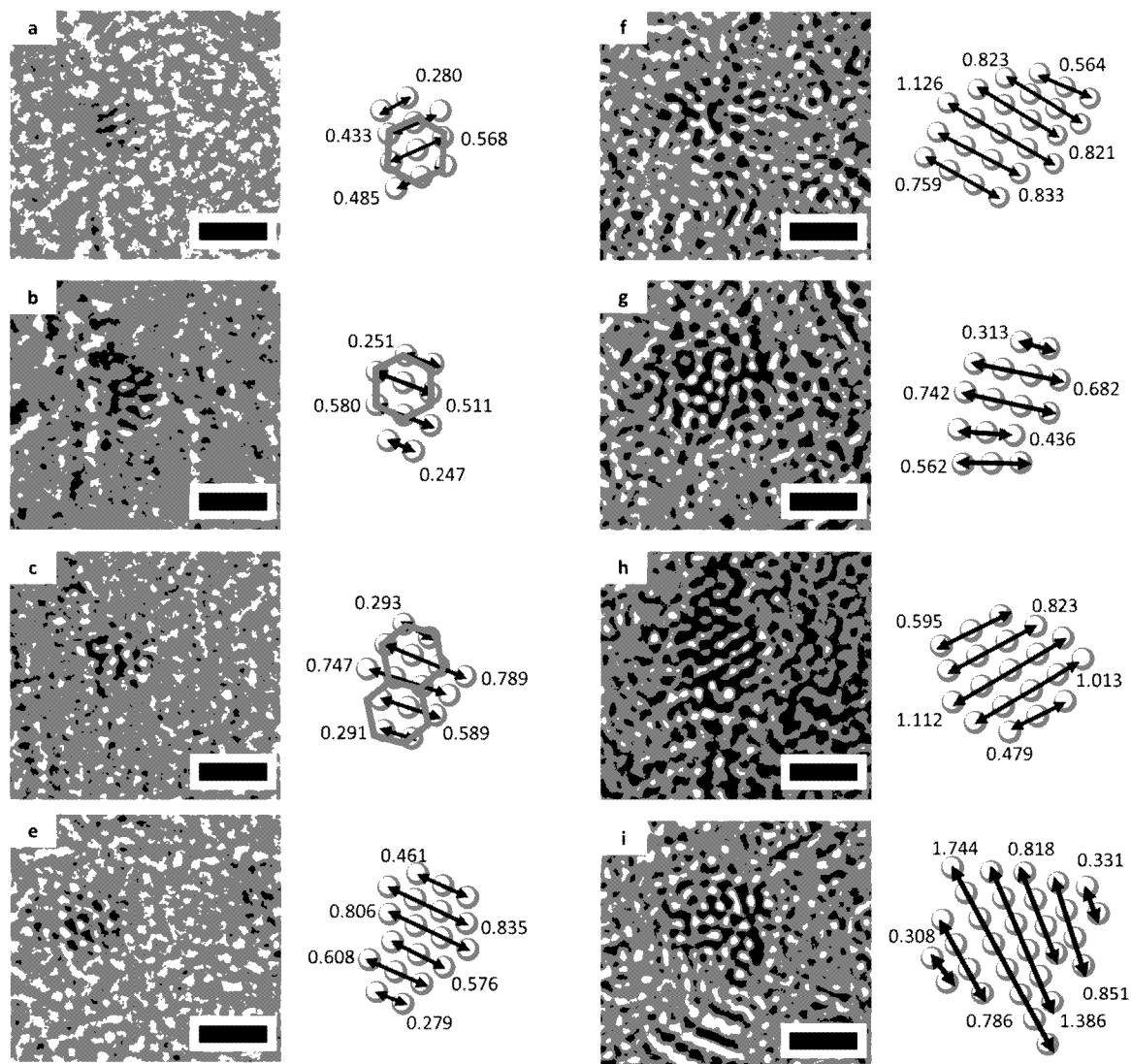


Figure 22

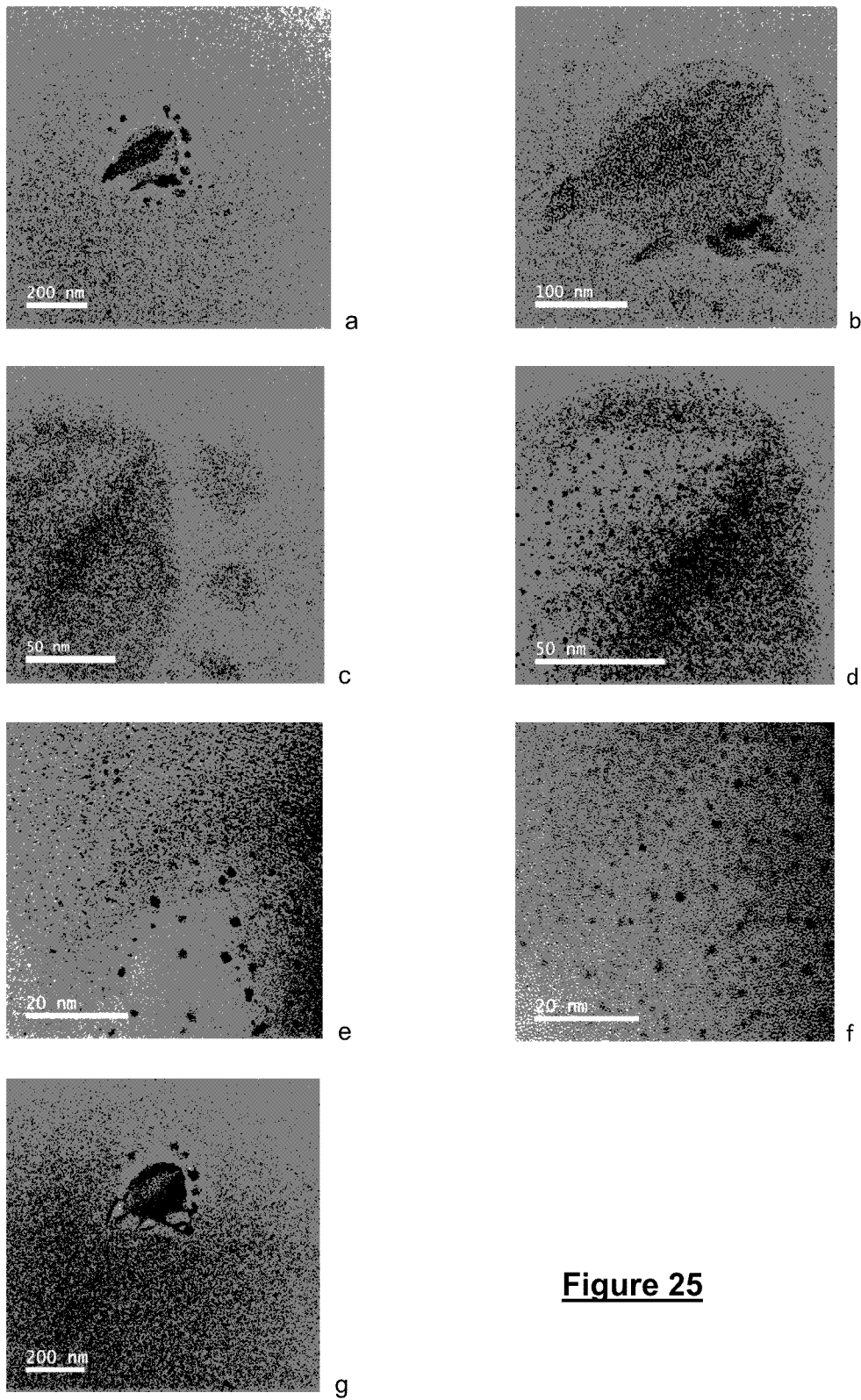
21/24

**Figure 23**

22/24

**Figure 24**

23/24

**Figure 25**

24/24

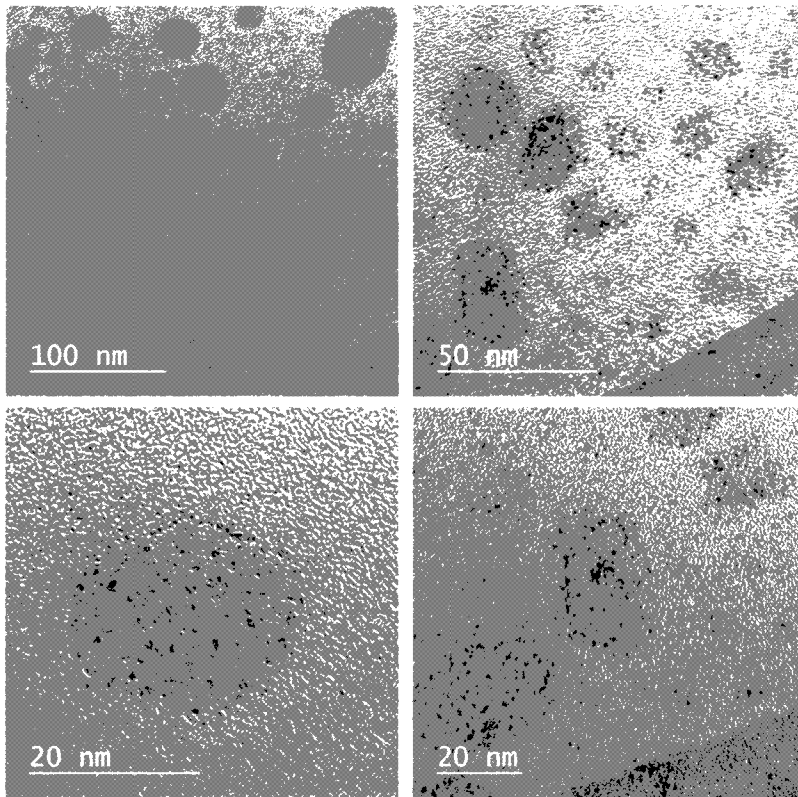


Figure 26

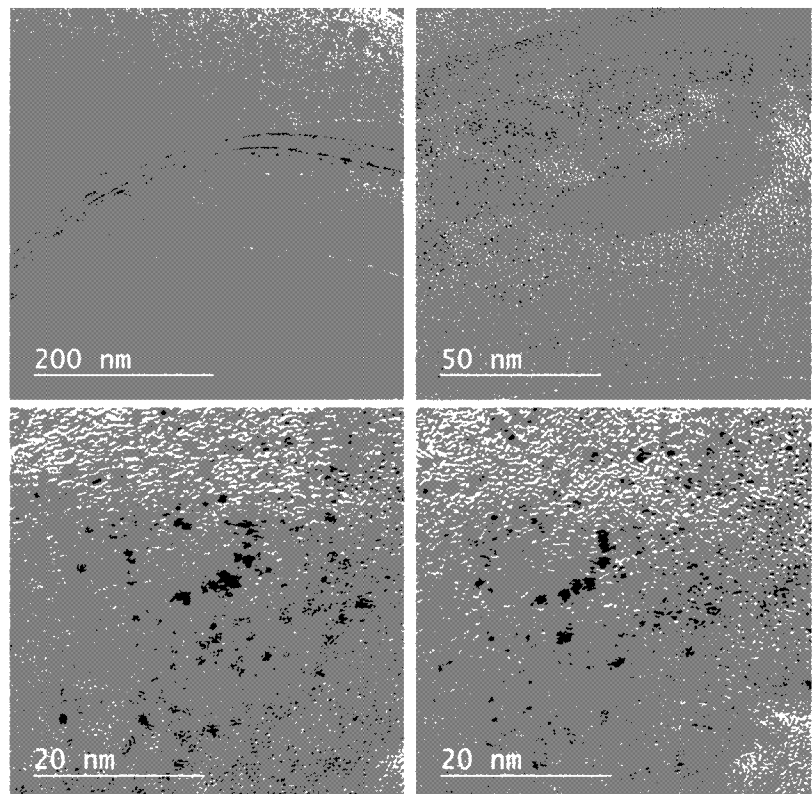


Figure 27

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2015/051264

A. CLASSIFICATION OF SUBJECT MATTER
INV. B22F1/00 B22F9/24
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, INSPEC, COMPENDEX, EMBASE, FSTA, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YOON HEE JANG ET AL: "The fabrication of graphitic thin films with highly dispersed noble metal nanoparticles by direct carbonization of block copolymer inverse micelle templates", CARBON, ELSEVIER, OXFORD, GB, vol. 49, no. 6, 19 January 2011 (2011-01-19), pages 2120-2126, XP028153279, ISSN: 0008-6223, DOI: 10.1016/J.CARBON.2011.01.049 [retrieved on 2011-01-25]	1-9, 13-26
A	page 2121, left-hand column, paragraph 3 2.2. Fabrication of the hybrid metal/carbon thin films; page 2121 figure 2(h) ----- -/-	10-12, 27-39



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

9 July 2015

Date of mailing of the international search report

17/07/2015

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Helgadóttir, Inga

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2015/051264

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LI J ET AL: "Reverse micelles of star-block copolymer as nanoreactors for preparation of gold nanoparticles", POLYMER, ELSEVIER SCIENCE PUBLISHERS B.V, GB, vol. 47, no. 26, 8 December 2006 (2006-12-08), pages 8480-8487, XP028061225, ISSN: 0032-3861, DOI: 10.1016/J.POLYMER.2006.09.071 [retrieved on 2006-12-08]	27,29, 32,33
Y	Scheme 2	28,30,31
A	page 8485, left-hand column, paragraph 1	1-26, 34-39
X	----- MING-LI WU ET AL: "Synthesis of Au/Pd Bimetallic Nanoparticles in Reverse Micelles", LANGMUIR, vol. 17, no. 13, 1 June 2001 (2001-06-01), pages 3877-3883, XP055201300, ISSN: 0743-7463, DOI: 10.1021/la010060y	39
Y	Preparation of Nanoparticles;	30,31
A	page 3878, right-hand column Particle Structure; page 3879	1-29, 32-38
X	----- B. P. VINAYAN ET AL: "Solar light assisted green synthesis of palladium nanoparticle decorated nitrogen doped graphene for hydrogen storage application", JOURNAL OF MATERIALS CHEMISTRY A, vol. 1, no. 37, 1 January 2013 (2013-01-01), page 11192, XP055201321, ISSN: 2050-7488, DOI: 10.1039/c3ta12016c	34-38
A	2.1 Sample preparation; page 11193	1-33,39
Y	----- XIN THANG ET AL: "Water-in-Oil Microemulsion Synthesis of Platinum-Ruthenium Nanoparticles, Their Characterization and Electrocatalytic Properties", CHEMISTRY OF MATERIALS, AMERICAN CHEMICAL SOCIETY, US, vol. 15, 1 January 2003 (2003-01-01), pages 451-459, XP002491167, ISSN: 0897-4756, DOI: 10.1021/CM0344414 [retrieved on 2002-12-18]	28
A	Experimental Section; page 452	1-27, 29-39
	----- -/--	

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2015/051264

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 103 028 737 A (INST SEMICONDUCTORS CAS) 10 April 2013 (2013-04-10) page 2, paragraph [0020] - page 3, paragraph [0032] -----	1-39

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2015/051264

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 103028737	A	10-04-2013	NONE
