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Dynamics of formation of Ru, Os, Ir and Au metal nanocrystals on doped graphitic surfaces

Anaïs Pitto-Barry, Peter J. Sadler and Nicolas P. E. Barry*

The fabrication of precious metal (ruthenium, osmium, gold, and iridium) nanocrystals from single atoms has been studied in real-time. The dynamics of the first stage of the metal nanocrystallisation on a doped (B,S)-graphitic surface are identified, captured, and reported.

Metal nanocrystals offer considerable potential for applications in healthcare,1–5 electronics,4 and catalysis.5 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.6 The former relies on a progressive removal of material until the desired nanomaterial is obtained,7 whilst the latter uses atomic or molecular precursors and gradually assembles them until the desired structure is formed.8 Examples of physical and chemical techniques for the fabrication of Ru, Au, and Ir nanocrystals are summarised in Table 1.

Nanocrystallisation follows a three-stage approach: nucleation, evolution of nuclei into seeds, and growth of seeds into nanocrystals.32 Nucleation is the first step of any crystallisation process, evolution of nuclei into seeds, and growth of seeds into nanocrystals.32–41 Nonetheless, imaging the early stage of a nanocrystallisation process in real-time and in real-space is challenging and little is known about growth rates of nuclei, the minimuscle clusters made of a few atoms formed in the earliest stage of nanocrystal synthesis.

We have recently developed a new technology based on transmission electron microscopy, which allows the direct observation, in real-time, of atom-by-atom fabrication of metal nanocrystals.42–44 This methodology involves electron beam irradiation of metallated micelles with an aberration-corrected high-resolution transmission electron microscope (AC-TEM). Upon irradiation, the micelles form a doped graphitic support on which individual metal atoms hop and migrate to form nanocrystals, as small as 15 Å in diameter in less than 1 h. As an initial example, we observed, quantified, and controlled the growth of osmium nanocrystals in real time. Using this methodology, we report here the fabrication of gold, ruthenium, and iridium nanocrystals, precious metal nanoparticles. We capture the aggregation of individual atoms to form nuclei. The nanocrystallisation growth rate is determined for each precious metal, providing new insights into the nucleation step of nanocrystal formation. We prepared block copolymer micelles containing 16-electron dithiocarbamato complexes of Ru(II), Os(II), Ir(III) or Au(III) (Fig. 1), 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 cm−2; 7.6 × 107 electrons nm−2 s−1).

OsMs and RuMs micelles containing [Os/Ru(η-cymene)(1,2-dicarba-closo-dodecaborane-1,2-dithiolate)] encapsulated in triblock copolymer Pluronic® P123 were synthesised following our reported procedure,44,45 while the Au-containing AuMs and Ir-containing IrMs micelles were synthesised following a similar procedure (see Materials and methods). To ensure first that the micelle degradation leads to the formation of metal nanocrystals for each metal, we irradiated the TEM grids for up to 150 min. As previously reported with OsMs, we observed structural changes within the Pluronic® film formed by the spreading of RuMs, AuMs, and IrMs within the holes of lacey carbon TEM grids upon irradiation with the high-energy electron beam. The emergence of atomic ordering within the self-supporting matrix consistent with a turbostratic graphitic structure was apparent within a few minutes. Along with these structural modifications of the self-supporting polymeric film, a rapid decomposition of the carborane-containing Ru, Au, and Ir complexes was also observed (in less than 1 min), and precious metal nanoparticles were imaged after 120 min (Fig. 2).

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Significantly, the in situ-generated precious metal nanoparticles on the self-supporting graphitic matrix are crystalline. This is illustrated by the FFT analysis (Fig. 2) of the ca. 1.5 nm-diameter Os, Ru, Au, and Ir nanocrystals depicted in Fig. 2. Such observations not only generalise this atom-by-atom fabrication methodology to a range of precious metals, but also show that various types of metal complexes can be used as precursors. The pseudo-octahedral Ru(n) complex is a half-sandwich organometallic arene complex (structurally analogous to the Os(n) precursor), whereas the half-sandwich Ir(III) complex has a cyclopentadienyl ligand, whilst the Au(n) complex has a square-planar geometry and is not an organometallic compound. Hence it is evident that the presence of an aromatic ring in the chemical structure of the precursor complex is not needed to generate the underlying graphitic support or induce formation of nanocrystals using this methodology, nor is having an octahedral complex as precursor. This work suggests that the methodology is also likely to be successful using other square-planar precious metal complexes such as Pd(II) and Pt(II) as precursors. The ability to control the formation of very small (ca. 1.5 nm diameter) Au nanocrystals is particularly significant in view of current intense interest in catalysis, sensing, and quantum plasmonics. 46,47

We then imaged the early steps of nuclei aggregation for each metal (Table 2 and Fig. 3). The metal–metal distances for Au, Os, Ir, and Ru were first measured on small molecules

Table 1 Examples of Ru, Ir, and Au nanocrystal fabrication techniques

<table>
<thead>
<tr>
<th>Metal</th>
<th>Fabrication technique</th>
<th>Year</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>Chemical reduction</td>
<td>2012, 2013</td>
<td>9–11</td>
</tr>
<tr>
<td></td>
<td>Thermal reduction</td>
<td>2011</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Thermal reduction on carbon-based substrates</td>
<td>2011</td>
<td>6–17</td>
</tr>
<tr>
<td></td>
<td>Chemical decomposition</td>
<td>2005</td>
<td>13, 14</td>
</tr>
<tr>
<td></td>
<td>Microwave irradiation</td>
<td>2011</td>
<td>15–17</td>
</tr>
<tr>
<td>Ir</td>
<td>Seed-mediated growth</td>
<td>2014</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Atomic layer deposition</td>
<td>2014</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>Chemical reduction</td>
<td>2009, 2014</td>
<td>20–22</td>
</tr>
<tr>
<td></td>
<td>Thermal annealing process</td>
<td>2010</td>
<td>23</td>
</tr>
<tr>
<td>Au</td>
<td>Thermal treatment</td>
<td>2009, 2014</td>
<td>24, 25</td>
</tr>
<tr>
<td></td>
<td>Nanopatterning: seed-mediated growth with a surfactant</td>
<td>2013</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>Colloidal lithography and surface energy-driven dewetting process</td>
<td>2013</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>DNA-mediated self-assembly</td>
<td>2013</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Light-induced rapid annealing</td>
<td>2014</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>Chemical reduction</td>
<td>1994, 2009</td>
<td>30, 31</td>
</tr>
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Ru, Au, and Ir nanocrystals depicted in Fig. 2. Such observations not only generalise this atom-by-atom fabrication methodology to a range of precious metals, but also show that various types of metal complexes can be used as precursors. The pseudo-octahedral Ru(n) complex is a half-sandwich organometallic arene complex (structurally analogous to the Os(n) precursor), whereas the half-sandwich Ir(III) complex has a cyclopentadienyl ligand, whilst the Au(n) complex has a square-planar geometry and is not an organometallic compound. Hence it is evident that the presence of an aromatic ring in the chemical structure of the precursor complex is not needed to generate the underlying graphitic support or induce formation of nanocrystals using this methodology, nor is having an octahedral complex as precursor. This work suggests that the methodology is also likely to be successful using other square-planar precious metal complexes such as Pd(II) and Pt(II) as precursors. The ability to control the formation of very small (ca. 1.5 nm diameter) Au nanocrystals is particularly significant in view of current intense interest in catalysis, sensing, and quantum plasmonics. 46,47

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Table 2 Precious metal nanocrystal growth parameters

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<td>Nanocrystal</td>
<td>Bulk^{30,31}</td>
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<tr>
<td>Ru</td>
<td>0.248 ± 0.072</td>
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</tr>
<tr>
<td>Os</td>
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Fig. 1 (a) Self-assembly of block copolymer micelles containing encapsulated metal (Os, Ru, Ir, or Au) carborane complexes. (b) The methodology used in this work is the following: (1) electron beam irradiation of the metallated micelles; (2) degradation and production of a graphenic surface (without attempt to indicate B and S doping) on which individual metal atoms can hop and migrate; (3) metal nucleation and formation of small molecules, clusters; (4) metal nanocrystal formation.

Significantly, the in situ-generated precious metal nanoparticles on the self-supporting graphitic matrix are crystalline. This is illustrated by the FFT analysis (Fig. 2) of the ca. 1.5 nm-diameter Os, Ru, Au, and Ir nanocrystals depicted in Fig. 2. Such observations not only generalise this atom-by-atom fabrication methodology to a range of precious metals, but also show that various types of metal complexes can be used as precursors. The pseudo-octahedral Ru(n) complex is a half-sandwich organometallic arene complex (structurally analogous to the Os(n) precursor), whereas the half-sandwich Ir(III) complex has a cyclopentadienyl ligand, whilst the Au(n) complex has a square-planar geometry and is not an organometallic compound. Hence it is evident that the presence of an aromatic ring in the chemical structure of the precursor complex is not needed to generate the underlying graphitic support or induce formation of nanocrystals using this methodology, nor is having an octahedral complex as precursor. This work suggests that the methodology is also likely to be successful using other square-planar precious metal complexes such as Pd(II) and Pt(II) as precursors. The ability to control the formation of very small (ca. 1.5 nm diameter) Au nanocrystals is particularly significant in view of current intense interest in catalysis, sensing, and quantum plasmonics. 46,47

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Fig. 2 AC-TEM images of Ru, Os, Ir, and Au nanocrystals (with corresponding fast Fourier transform) on a turbostratic graphitic structure obtained after 120 min electron beam irradiation. Scale bar 1 nm.

Fig. 3 Atom-by-atom growth of Ru (left) and Au (right) nanocrystals over time and interatomic distances within nuclei. Scale bar 1 nm.
example, the high affinity of sulfur for gold is well-known, and strong Au–S interactions might explain the slow rate of nanocrystal formation observed for Au compared to Os, and Ru, with Au atoms perhaps being tightly trapped on the S sites. The Au precursor is also the only complex in the series studied with two carborane ligands in its molecular structure, and therefore, the graphitic support is likely to be doped with more B and S atoms than those formed by irradiation of micelles OsMs, RuMs, and IrMs. Differences in metal–metal affinity might also have a marked effect on the rate of nucleation. The aurophilicity, or tendency of gold aggregation via gold–gold interactions, is expected to have a direct impact on the nucleation, but would be expected to facilitate the formation of Au nanocrystals. Such relativistic effects might also occur with the heavy Ir atoms, however, Ir nanocrystals have the slowest formation rate. These observations will stimulate future work combining further experiments on nanocrystal nucleation with advanced calculations and modelling.

The high-energy electron beam of high-resolution (HR) TEM is not only a powerful analytical tool but may be also utilised as an external force to modify in situ the structure and composition of various nano-scale materials, and to tailor the assembly of nanoparticles. For instance, gold nanoclusters have been extensively studied in situ in a wide variety of systems, including mixed metal alloys. Moreover, the kinetic energy of the electron beam is probably the main driving force for the observed dynamic behaviour of the metal atoms observed in TEM, and was set to be the same for all the experiments reported here (1.9 pA cm−2). This may explain the narrow range of crystal growth observed for each metal. The interactions of individual Ru, Os, Au, and Ir atoms with the underlying surface may also have a direct impact on the rates of nucleation. The in situ-produced via electron beam degradation of the metallated micelle precursors) graphic surface which supports the growth of the metal nanocrystals is doped with boron, and sulfur atoms (10–20 boron atoms for one metal ion, and 2–4 sulfur atoms per metal ion). These hetero-atoms can act as trapping sites for the single metal atoms, slowing down their motions on the surface, with a rate-dependency related to the nature of the metal and the doping atoms. For example, the high affinity of sulfur for gold is well-known, and strong Au–S interactions might explain the slow rate of nanocrystal formation observed for Au compared to Os, and Ru, with Au atoms perhaps being tightly trapped on the S sites. The Au precursor is also the only complex in the series studied with two carborane ligands in its molecular structure, and therefore, the graphitic support is likely to be doped with more B and S atoms than those formed by irradiation of micelles OsMs, RuMs, and IrMs. Differences in metal–metal affinity might also have a marked effect on the rate of nucleation. The aurophilicity, or tendency of gold aggregation via gold–gold interactions, is expected to have a direct impact on the nucleation, but would be expected to facilitate the formation of Au nanocrystals. Such relativistic effects might also occur with the heavy Ir atoms, however, Ir nanocrystals have the slowest formation rate. These observations will stimulate future work combining further experiments on nanocrystal nucleation with advanced calculations and modelling.

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HR-TEM: A JEOL JEM-ARM200F HR-TEM was operated at 80 keV, 1.9 pA cm\(^{-2}\), with spherical aberration (C\(_s\)) tuned to approximately +1 \(\mu\)m and images were recorded on a Gatan SC1000 Orius CCD camera. All the images were analysed with ImageJ (Fiji) software. All the stacks were aligned with the plugin software StackReg.\(^{37}\) The image sequences were independently aligned using a Digital Micrograph(TM) script. Adjacent images were aligned by analysis of the normalised cross-correlation of a user-selected region in the image stack. The centre of the cross-correlation peak was found to sub-pixel accuracy using either (a) the centroid of the correlation peak or (b) fitting of parabolas to the peak in \(x\) and \(y\) directions, while linear interpolation was used to produce sub-pixel image shift.

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Notes and references