

Interfacial Structures and Bonding in Metal-Coated Gold Nanorods

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Abstract We present a topical review of research in the field of metal-coated gold nanorods. By combining synthetic design strategies with state-of-the art characterisation techniques (particularly aberration-corrected scanning transmission electron microscopy) and molecular dynamic simulations, we demonstrate the potential to gain a fundamental understanding of, and control over, the atomic detail of metal–metal bonding at the interfaces of core–shell nanorods and nanoparticles. This analysis is facilitated by making comparisons between the related bimetallic systems: AuRh, AuPd and AuPt.

Keywords Bimetallic core–shell structures · Electron microscopy · Gold · Molecular dynamic simulations · Nanoparticles · Nanorods · Synthesis · Scanning transmission electron microscopy

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1 Introduction

Nanoalloys (NAs) are nanoscale clusters of two or more metallic elements. They can be generated in the vapour phase, in solution, on substrates or in matrices, with varying degrees of control over size, composition, structure and chemical ordering [1–4]. Nanoalloys are of great interest both for their unique chemical and physical properties and their tunability. For example, catalysis by NAs is a thriving area of research as the catalytic activity and/or selectivity of metal nanoparticles can often be dramatically improved as a result of synergistic interactions between the component metals in an alloy [5, 6].

Four main types of chemical ordering have been identified for NAs [7]. *Core-shell-segregated NAs* consist of a shell of one type of atom (B) surrounding a core of another (A), though there may be some mixing between the shells. *Layered-segregated NAs* consist of distinct A and B sub-clusters, such as so-called “Janus” particles [8]. *Mixed NAs* may be either ordered or random. *Multishell NAs* have onion-like alternating concentric -A-B-A- shells. Factors influencing chemical ordering include metal–metal bond strengths, surface energies, atomic size mismatch, charge transfer, substrate and surfactant binding and specific electronic or magnetic effects. The chemical ordering observed for a particular NA depends critically on the balance of these factors, as well as on the synthetic method and experimental conditions [7, 9].

The focus of this topical review is on a subset of core-shell nanoalloys, bimetallic nanorods (NRs). Rod-shaped nanoparticles, especially those of gold, have been extensively studied for their interesting opto-electronic properties, which can be varied by control of aspect ratio and metal distribution [10]. An additional advantage of the study of NRs is their more varied faceting compared with spherical nanoparticles, which is interesting for examining the growth pattern of one metal on another [10, 11].

The metal–metal interactions that drive the structure and properties of core-shell NAs are most concentrated at the buried core-shell interface. Thus understanding the nature and structures of these interfaces is of key importance for the effective exploitation of core-shell bimetallic NRs. In this review we summarise the current state of work in this topic. We compare three nanorod systems, employing examples drawn mainly from our recent investigations of the metal–metal interfacial structures

of Rh, Pd and Pt deposited on gold nanorods. We show how the balance between thermodynamic properties (e.g. surface energy, bulk cohesive energy), lattice constant and kinetics influences their structure and, consequently, properties and stability. Before presenting a detailed review of this work, we introduce briefly the synthetic strategies, characterisation techniques and computational methodologies employed.

2 Synthetic Strategies

The synthesis of nanoalloys for particular applications requires control over the size and shape of the nanoparticles as well as the distribution of the metals within them (e.g. core-shell vs solid solution). Fine control of size can be achieved through the use of cluster beam sources, which are typically used to investigate the effects of the sizes of mono-elemental clusters on their properties [12–14]. In some cases of bimetallic nanoclusters, the control of chemical ordering has also been successful [15, 16]. The high yield of clusters required for many potential applications using this approach is a challenge and the synthesis of NAs via wet chemical methods has been very widely used.

Control of size can also be achieved with wet chemical methods. A metal salt is reduced with a chemical reducing agent in the presence of capping agents, surfactants or ions and the temperature and concentrations of the species are varied [17, 18]. For example, the kinetics of reduction can be controlled by altering either the concentration of the metal salt or the relative rates of nucleation and growth by varying the concentration and identity of a capping agent [17].

Control of the shape of nanoparticles has also attracted much interest [18, 19]. The shape of Au nanoparticles has a profound influence on their optical properties [19–21] and the shape of particles also determines the crystal facets present, which influences their catalytic properties [22, 23]. Shape control has been most extensively studied for Au nanoparticles, with spheres, cubes [24, 25], triangles [25], prisms [25], bipyramids [26], polyhedra [27] and rods [19, 28] all being reported. The control of particle shape is generally achieved via seed-mediated growth methods, where additives, such as specifically adsorbing ions or metals and shape-forming surfactants, are used to control the relative rates of growth of particular facets [25, 29]. For example, cetyltrimethylammonium bromide (CTAB) is commonly employed in the synthesis of cubes and rods, whereas the use of the corresponding chloride generally generates spherical particles [21] and the inclusion of varying amounts of Ag^+ ions in solution has been utilised to control the shape of Au nanoparticles as a result of the differences in affinity of Ag metal for different facets of Au [25]. These methods have been reviewed and discussed elsewhere [21, 25, 29].

The synthesis of bimetallic or multimetallic nanoparticles is more complex, with a range of parameters determining the final distribution of the metals involved. Co-reduction of two metal salts can lead to alloying of the two metals or core-shell

distribution, depending on relative surface energies, cohesive enthalpies vs. mixing enthalpy, entropy and lattice constant [7]. Kinetics also influences the final structure as often one metal salt may be more readily reduced than another. To synthesise core-shell nanoparticles, where the desired structure is not the thermodynamically favoured structure, a species that favours binding to the desired “shell” metal can be added. For example, if Ag and Pd are co-reduced, clusters with Pd core and Ag shell normally result. If ammonia is added to the reaction mixture, its stronger binding to Pd than to Ag results in particles with Ag cores and Pd shells [30]. Similarly, PdRh structures can be controlled by varying the reaction conditions: the presence of oxygen favours an Rh-enriched shell, whereas the presence of carbon monoxide favours a Pd-enriched shell [31]. It should also be noted that the distribution of metals within nanoalloy catalysts can be affected during operation [31]. For example, PtNi nanoparticles have been shown with in situ X-ray absorption spectroscopy (XAS) and Density Functional Theory (DFT) to vary in surface composition, with enrichment of the surface in Ni during hydrogen adsorption [32]. An alternative means to achieve a core-shell structure that is the inverse of the thermodynamically favoured product is to synthesise seed nanoparticles of the “core” metal and to deposit the “shell” metal onto the seeds in a second step. This method is particularly useful when a particular shape is desired because shape control is simpler in monometallic systems. The wide variety of shapes and sizes available for gold nanoparticles makes gold core-M shell nanoparticles an ideal case study for the examination of the mechanism of the deposition of a metal shell onto pre-formed seed clusters.

3 Mechanisms for Metal-on-Metal Growth

To understand the complex structures that can form in bimetallic core-shell nanoparticles, one can start by studying the growth modes that may be followed by one metal deposited on the flat surface of another. Figure 1 shows a schematic example of three possible growth modes.

Considering only the key parameters of the relative lattice constants and bond strengths, Volmer-Weber island growth is expected in systems with a high lattice mismatch and low tendency to form inter-metallic bonds and layer-by-layer Frank van der Merwe growth in systems with a low lattice mismatch and a high preference for inter-metallic bonds [33]. However, for systems between these extremes, growth modes can become more complex, such as Stranski-Krastanov layer-plus-island growth, wherein a tendency to form inter-metallic bonds initially favours layer growth but accumulated strain caused by lattice mismatch then induces a second phase of 3D island growth. The point at which the growth changes from layer to island depends upon the balance between bond strength and lattice strain, so the exact growth mode followed by any given system may not be easy to predict, even in this simplified example. In real systems, the range of influencing factors is greater, for example, layered overgrowth can occur even when there is significant lattice mismatch by proceeding in a different orientation or with a different crystal

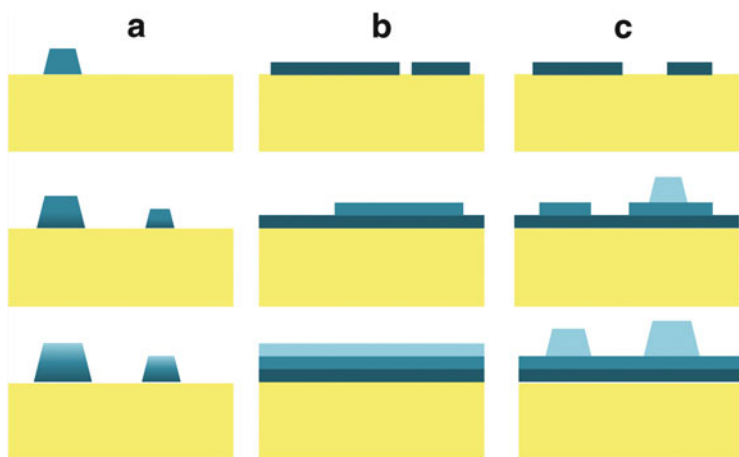


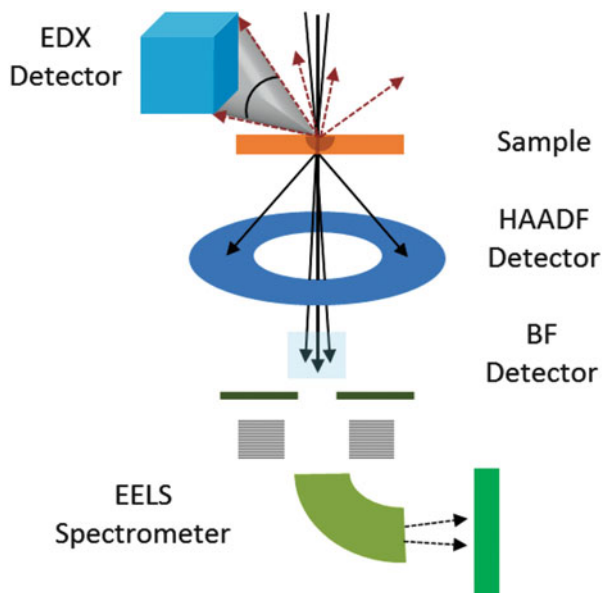
Fig. 1 Simple scheme for the categorisation of growth modes. (a) Volmer–Weber island growth, (b) Frank van der Merwe layer-by-layer growth and (c) Stranski–Krastanov layer-plus-island

structure to the substrate [34] or through the formation of systematic defects to relieve lattice strain [35].

Other parameters that may also be important for the formation of particular structures in bimetallic systems include the relative surface energies of the constituent metals, their respective rates of surface diffusion, the conditions prevailing during or after deposition and the existence of non-flat surfaces. These vary considerably between systems; for example, lattice mismatch can range from almost no mismatch in a system such as AuAg to a mismatch as great as 12% between Cu and Ag [36]. In addition, while lattice mismatch might be the principal driving factor for one size or structure of particle in one bimetallic system, other parameters such as surface or cohesive energy may override the influence of lattice mismatch and become more dominant for others. The wealth of influencing factors makes complete structural prediction a more challenging task in these systems; however, it gives more potential routes to manipulating structure and thus properties. For example, Au and Pd are miscible in bulk form [37], but AuPd nanoparticles have been synthesised with both segregated [38–41] and alloyed [39, 42] structures, by varying synthesis conditions. Transformations between these structures have been linked to variations in catalytic reactivity and can be induced by heating the samples [42].

For core–shell nanoparticles, the metal–metal interactions occur predominantly in sub-surface sites, at their buried interfaces. The interfacial structures of core–shell systems could influence their surface structure if the shell is thin, and thus their surface properties [43]. The connection between core–shell structure and resulting properties has been demonstrated by recent work conducted on AgPd [44] and PtNi [45] nanoparticles, where enhanced catalytic reactivity was attributed to the influence of lattice strain at the core–shell interface. Core–shell structure has also been

Fig. 2 Scanning transmission electron microscope (STEM) imaging detectors and spectrometers. Schematic diagram illustrating the location of the high angle annular dark field (HAADF) and bright-field (BF) imaging detectors and the energy dispersive X-ray (EDX) and electron energy loss spectroscopy (EELS) spectrometers. Reproduced from [49]



found to impart additional stability to nanoparticles, delivering greater durability compared with monometallic equivalents, which is an important factor in many industrial applications [46].

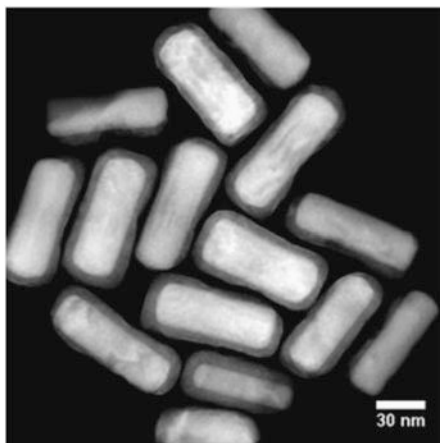
4 Characterisation Techniques

Gaining fundamental understanding of the driving forces behind the properties of bimetallic nanoparticles requires the use of techniques that are capable of obtaining atomically resolved elemental detail from sub-surface locations. *Aberration-corrected scanning transmission electron microscopy (ac-STEM)* is one of the few techniques with the potential to carry out this work [47, 48]. It has the capability to obtain a wide range of characterisation data, with atomic resolution and single-atom sensitivity, in a single instrument.

4.1 Imaging

STEM employs a focussed probe of electrons scanned across an area of a sample. Figure 2 shows a schematic representation of the principal detectors used in ac-STEM that can be employed to collect both elemental and structural data.

Fig. 3 STEM-HAADF image showing Z-contrast between the segregated Au core and Pd shells. Reproduced from [51]. Reproduced by permission of the Royal Society of Chemistry. [For the electronic version: <http://dx.doi.org/10.1039/C3NR02560H>]



The high-angle annular dark-field (HAADF) detector collects electrons that are scattered to wider angles through interaction with the sample. These scattered electrons can be regarded as incoherent. The cross section of the incoherently scattered electrons depends on mainly sample thickness and the atomic numbers of the elements, which makes interpretation of HAADF image contrast relatively straightforward [50]. Where the sample is of uniform thickness, HAADF image contrast variation can be directly related to sample elemental variation. Figure 3 shows a typical HAADF image of segregated AuPd nanorods [51], demonstrating a clear difference in image intensity between the Au core ($Z = 79$) and the Pd shell ($Z = 46$).

In addition to the HAADF detector, ac-STEM also has the capability for bright-field (BF) imaging through the detection of electrons scattered to small forward angles by the sample, and, as such, assumed to retain their coherence. BF image contrast can be related to phase changes caused by interactions between the beam electrons and the sample. They are sensitive to extremely fine structural detail, such as the presence of lattice strain, and are also more affected by lighter elements, such as the amorphous carbon substrate of TEM grids, than DF images. Figure 4 shows simultaneously acquired STEM-HAADF and STEM-BF “as taken” images from the edge of an Au nanorod and illustrates the difference between DF amplitude contrast images and BF phase contrast images. Atomic resolution is apparent in both images; however, the greater sensitivity of BF imaging to lighter atoms means the grain of the underlying amorphous carbon support is apparent in the BF image but not in the HAADF image.

Imaging information can be maximised by using the two detectors simultaneously. This allows the simplicity of HAADF interpretation to aid interpretation of more complex BF images, while the finer structural detail available in BF images can complement the superior atomic resolution of HAADF images. Recently, Goris et al. further demonstrated the potential of ac-STEM in the characterisation of core-shell interfaces by employing tomography techniques to examine the core-shell AuAg nanorods from several different imaging angles [52]. Although tomography

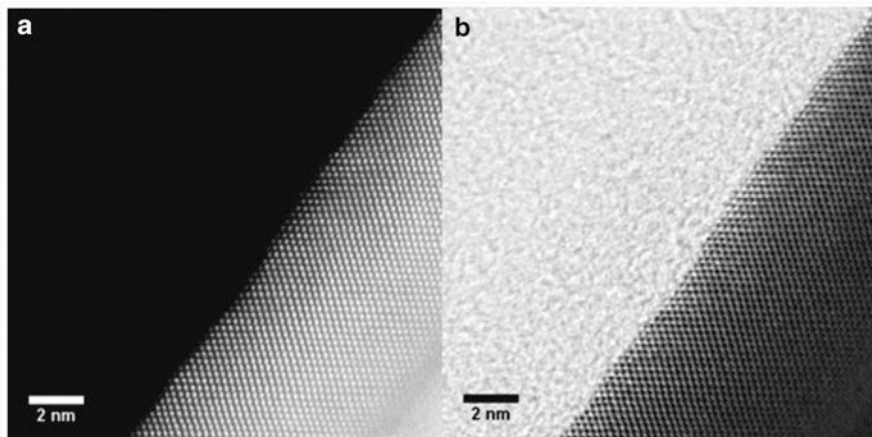


Fig. 4 Simultaneously acquired STEM-HAADF (a) and STEM-BF (b) images taken from the edge of an Au nanorod. Reproduced from [49]

is a time-consuming process, this study showed that it can be used to build a 3D representation of interfacial structure in individual bimetallic nanoparticles.

4.2 Spectroscopy

Energy-dispersive X-ray spectroscopy (EDX) is a form of spectroscopy that utilises the detection of X-ray emissions that occur when beam electrons interact with the sample. These X-ray emissions are entirely elementally specific. Given sufficient X-ray counts, statistical methods can be used to calculate accurately the relative quantities of elements present in the sample from EDX spectra [53]. The technique of elemental mapping is particularly useful for analysing bimetallic samples and has been used extensively in this regard.

In contrast to EDX, electron energy loss spectroscopy (EELS) tends to have a better signal to noise ratio, thus improving spatial resolution. EEL spectra show the energy lost by individual beam electrons as they are transmitted through the sample. As the electronic interactions are derived from the dielectric response, they are elementally specific [54]. Thus EELS can be an effective tool to measure the elemental composition of bimetallic samples, particularly when used in combination with elementally sensitive STEM-HAADF imaging. The better signal to noise ratio of EELS compared to EDX results in improved spatial resolution. However, in comparison to EDX, EELS spectra can be more complex to interpret, as the position and appearance of spectral features can be affected by the electronic structure of the sample. EELS is also limited to signals that are within the range of the spectrometer and so is of less use in measuring high energy loss signals (over 1,000 eV energy loss), which is typically the case for core loss signals of heavier elements such as Au. For these signals, EDX is the preferred technique.

5 Computational Methods

In the field of nanoalloys, computer simulation is becoming increasingly important, both to predict the structures that may form through metal–metal interactions in bimetallic nanoparticles and to support the interpretation of experimental data.

While high-level *ab initio* molecular orbital calculations, including electron correlation, have been carried out for small nanoalloys with up to around ten atoms [55], owing to their computational expense, they rapidly become unfeasible for larger clusters. DFT calculations [56, 57], which scale much better with cluster size than *ab initio* methods, while typically showing good agreement with experiment, have become increasingly popular for studies of NAs with tens or even hundreds of atoms [58, 59], though rigorous structural searches at the DFT level (typically combined with genetic algorithm and basin-hopping Monte Carlo methods) have only been performed for smaller particles with up to around 20–30 atoms [60].

For this reason, studies of large NAs have tended to use computationally cheaper empirical atomistic potential energy functions, which do not explicitly include electronic effects. There are a variety of empirical atomistic potentials which have been applied to study the structures, dynamics and thermodynamics of NAs [7, 61]. These empirical potentials typically have parameters which are fitted to experimental (or high-level theoretical) data for bulk metals and alloys and sometimes for small clusters. There are several empirical many-body potentials based on the second moment approximation to tight-binding theory [62], the most widely applied for studying NAs being the Gupta potential [63, 64]. This potential has been used to study static and dynamic properties of NAs with hundreds or thousands of atoms [58, 65–68].

In the Gupta potential [63, 69], the configuration energy of a system of N atoms is obtained as

$$E = \sum_{i=1}^N (E_i^R + E_i^B) \quad (1)$$

where the contribution of each atom, i , comprises two terms:

$$E_i^R = \sum_{j \neq i}^N A \cdot \exp \left[-p \left(\frac{r_{ij}}{r_0} - 1 \right) \right] \quad (2)$$

$$E_i^B = - \sqrt{\sum_{j \neq i}^N \xi^2 \exp \left[-2q \left(\frac{r_{ij}}{r_0} - 1 \right) \right]} \quad (3)$$

The repulsive term, E_i^R , is the pairwise Born–Mayer-type interaction of atom i with its neighbours. The binding or cohesive term, E_i^B , is proportional to the width (square root of the second moment) of the d-band of the electron density of states,

Table 1 Key parameters for Rh, Pd, Pt and Au

	Rh	Pd	Pt	Au	Reference
Atomic number	45	46	78	79	[36]
Lattice constant (Å)	3.80	3.89	3.92	4.08	[36]
Average surface energy (J m ⁻²)	2.7	2.0	2.5	1.5	[72]
Bulk cohesive energy (eV atom ⁻¹)	5.75	3.89	5.84	3.81	[36]
Au–M diatomic binding energy (eV)	2.03	1.90	1.81	1.55	This study ^a

^aThe Au–M diatomic binding energies have been calculated at the LDA–DFT (PAW) level using the VASP package [73, 74]

expressed in terms of the so-called hopping integrals, ξ , between atom i and its neighbours. This term incorporates the many-body nature of the interaction. All interactions are assumed to decay exponentially with the interatomic distance r_{ij} . The parameters $\{A, \xi, p, q\}$ depend on the nature of the two atoms. Three parameter sets are thus needed for a binary system: two sets for the two homonuclear interactions and one for the heteronuclear interaction.

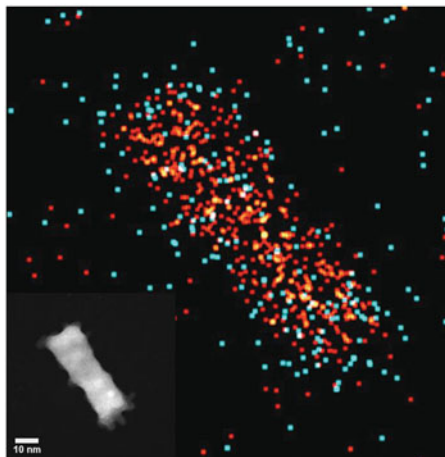
Typically, the parameters of the homonuclear interactions are fitted to reproduce the experimental values of the cohesive energy of the metal and its elastic constants. As a first approximation, the parameters of the heteronuclear interaction can be taken as the mean values of the corresponding parameters of the two elements. Although, in many cases, this has proved to be a successful strategy [70], a better representation of the mixing properties of the two elements can be achieved by fitting the heteronuclear parameters to the dissolution energies of each element into a bulk matrix of the other [71].

6 Case Studies of AuM Nanorods (M=Rh, Pd or Pt)

Gaining a fundamental understanding of the origin of the nanoscale properties of bimetallic nanoparticles is a challenging issue. We describe our recent work on three AuM systems, where M is Rh, Pd or Pt, to illustrate how the application of experimental structural characterisation, computer simulation and chemical synthesis techniques is possible to gain an understanding of, and control over, the factors that drive the formation of the interfacial structure in core–shell nanorods.

Key structural and energetic parameters for the elements Rh, Pd, Pt and Au are summarised in Table 1. These parameters, and the relative differences between them for the constituent metals of each system, underpin the metal–metal interactions that are instrumental in the formation and stability of structure through metal-on-metal growth.

Fig. 5 EDX maps of Au (red dots) and Rh (blue dots) taken from a AuRh nanorod. The insert is the STEM-HAADF image of the nanorod. Reproduced from [80]. Copyright 2012 American Chemical Society



6.1 Characterisation of Interfacial Structures of AuRh and AuPd Nanorods

The deposition of Rh on Au-seeded nanorods is of interest, partly because of the contrasting physical and chemical properties of these two elements. While Rh is catalytically active in the bulk form, Au has only been found to demonstrate catalytic activity in nanoscale systems. From Table 1, it can be seen that the large 7% lattice mismatch and the higher bulk cohesive energy and surface energy of Rh compared with Au suggest a preference for the $\text{Rh}_{\text{core}}\text{Au}_{\text{shell}}$ configuration. This has indeed been observed for nanoparticles formed on $\text{TiO}_2(110)$ surfaces by physical vapour deposition of either Rh followed by Au or vice versa [75, 76]. In these studies, the morphology of the bimetallic nanoparticles was examined using scanning tunnelling microscopy, while the chemical composition was characterised with low-energy ion scattering. Both techniques are surface sensitive; hence, information about the metal–metal interaction at the sub-surface region is rather limited. Despite the complete immiscibility of Au and Rh in the bulk [77], chemical synthesis of both segregated [78] and alloyed AuRh NAs [79] has also been reported.

In order to gain mechanistic understanding of metal–metal interactions at the atomic level, we have applied aberration-corrected STEM, as described in Sect. 4, to AuRh nanorods synthesised using a seed-mediated sequential growth method via a wet chemical route. The main results have been reported in two recent publications [51, 80]. Figure 5 shows EDX maps of Au and Rh overlaid on the same image. Despite the limited EDX counts, a clear correlation in the pattern of Au and Rh signals supports the formation of the $\text{Au}_{\text{core}}\text{Rh}_{\text{shell}}$ structure. As discussed in Sect. 3, a system of Rh sequentially deposited onto Au nanorods may not be in thermodynamic equilibrium. The atomic details at the interface can be revealed by simultaneously acquired DF and BF STEM images, shown in Fig. 6a, b, respectively, from

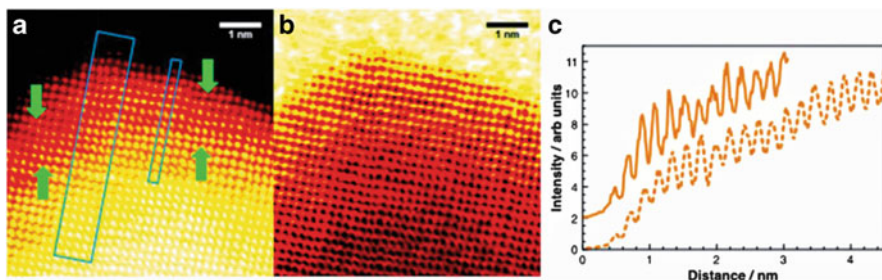


Fig. 6 Atomically resolved STEM-HAADF and BF images of the Au-Rh interface. Simultaneously acquired (a) STEM-HAADF and (b) STEM-BF images of an $\text{Au}_{\text{core}}\text{Rh}_{\text{shell}}$ nanorod, with (c) line intensity profiles taken as indicated in (a) over 4 atomic columns (70 pixels) and a single atomic column (16 pixels). Reproduced from [49]

the end of an AuRh rod. Although atomic columns are clearly resolved, there is no clear Z-contrast intensity variation as expected for Au ($Z = 79$) and Rh ($Z = 46$). Instead, random intensity variation from column to column is seen, as indicated by arrows in Fig. 6a, or more clearly by the intensity profiles shown in Fig. 6c. This result can be interpreted as a sign of intermixing or alloying at the interface. Further evidence can be seen below from the comparative study of Pd on Au nanorods. In addition, the atomic column spacing from the centre to the edge of the nanorod remains consistent with the Au lattice spacing, despite the 7% lattice mismatch between Rh and Au (see Table 1). Furthermore, there is no phase contrast feature in the AuRh BF image, suggesting that any mismatch strain may have been relieved by intermixing at the Au-Rh interface. The sequential method followed in synthesising these nanorods means that any mixing should have happened during or immediately after Rh deposition.

In contrast to AuRh, Z-contrast intensity variation is seen for AuPd nanorods, as shown earlier in Fig. 4. Here, comparable atomically resolved DF and BF images taken from a corner of an AuPd nanorod are displayed in Fig. 7a, b, where an abrupt contrast change is apparent that is consistent with the presence of a strain contrast feature in the BF image. This suggests that Au and Pd are well segregated, although Au and Pd are readily miscible in the bulk [37]. Core-shell segregation has been observed in other studies of AuPd nanoparticles synthesised using similar seed-mediated sequential methods [35, 38, 81].

Given that Rh and Pd have comparable atomic numbers, 46 vs 47, the clear difference in Z-contrast imaging obtained for these two systems highlights the difference in metal-metal interaction at the interfaces. The comparative approach adopted in this study of two systems with similar relative differences in key structural and elemental parameters (Table 1) highlights the important interplay between energetics, kinetics and thermodynamics in bimetallic nanostructure formation and shows the considerable potential that exists for structural manipulation through controlling kinetic parameters during synthesis. However, the driving force responsible for the interfacial structure of any given system cannot easily be determined by simply considering these parameters in isolation, so we have used

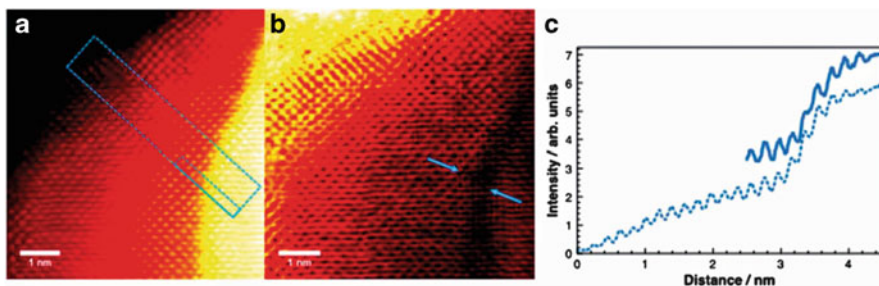


Fig. 7 Atomically resolved STEM-HAADF and BF images of the Au-Pd interface. Simultaneously acquired (a) STEM-HAADF and (b) STEM-BF images of an $\text{Au}_{\text{core}}\text{Pd}_{\text{shell}}$ nanorod, with (c) line intensity profiles taken as indicated in (a). Reproduced from [51]. Reproduced by permission of the Royal Society of Chemistry. [For the electronic version: <http://dx.doi.org/10.1039/C3NR02560H>]

computer simulations to assist with the analysis and interpretation of the experimental results. In addition to the AuPd and AuRh systems mentioned above, we have also considered the related AuPt system, for which structural and chemical studies have recently been carried out [82, 83].

6.2 Simulations of Deposition of Rh, Pd and Pt on Au Surfaces

The characteristic length of metal-coated nanorods is of the order of tens of nanometres. Modelling of deposition on flat surfaces should therefore be representative of the key processes occurring at the interface between the nanorod and the coating material during the process of deposition.

The computational studies reported below are based on molecular dynamic (MD) simulations, using the Gupta potential, of the deposition of metal atoms, Rh, Pd or Pt, onto an Au surface (henceforth denoted M/Au), in order to explore the initial stages of interfacial structure formation in these systems. The most instructive crystallographic orientations for simulation are the two low-index {111} and {100} orientations, because they typically have the lowest surface energies.

The Gupta potential parameter sets adopted for our simulations were taken from the literature. The Rh and Au parameters were taken from [63, 84] for Rh and Au, respectively, and the mixed interaction parameters were fitted to experimental dissolution energies of each element in a matrix of the other [77] (Ferrando R (2013) Personal communication). The AuPd parameters were taken from [85, 86]. Finally, the Au and Pt parameters were taken from [63], while the heteronuclear AuPt parameters were derived as the mean of the corresponding Au and Pt parameters [70].

The Nosé–Hoover thermostat [87] was applied in all MD simulations in order to maintain a constant temperature throughout the deposition process. Au {100} and

{111} slabs were modelled using six atomic layers, the bottom one being fixed at mean bulk positions, while the atoms of the other five layers are free to experience thermal motions. Each crystallographic plane contains 128 and 90 atoms for the {100} and {111} orientations, respectively. The thermal expansion of Au predicted by the Gupta potential was used to set the lattice constant for a given temperature. A deposition rate of 1 atom/ns was applied. Figure 8 shows snapshots from the MD simulations of the deposition of 1 monolayer (ML) of metal M (M=Rh, Pd and Pt) on both the {100} and {111} Au surfaces, for temperatures of 300 and 500 K.

6.2.1 Rh/Au

From the first column in Fig. 8, it is evident that Rh forms surface clusters on the Au substrate. Their average size depends on the surface mobility of the adatoms (and on the deposition rate). For instance, two sub-clusters can be distinguished for {100}/300 K, where the surface mobility is relatively low because of the low temperature and the higher coordination of an adatom on the {100} surface compared with the {111} surface. The surface cluster is more compact at $T = 500$ K. A single Rh cluster is observed on the {111} substrate for both temperatures. The formation of 3D Rh clusters on Au surfaces is consistent with the strong immiscibility of the two elements in the bulk. If low-coordinated Au atoms exist on the surface, they display a tendency to attach themselves to the Rh clusters and to climb onto their surface. The illustration at the bottom of column 1 of Fig. 8 shows a snapshot of a Rh cluster on the Au{111} substrate annealed at 500 K for 20 ns together with 8 Au adatoms. This effect, which is consistent with the Au–Rh exchange previously observed [75, 88, 89], results from the greater Au–Rh bond strength compared with that of the Au–Au bond and the much lower surface energy of Au than Rh (Table 1). If low-coordinated Au atoms are present on the surface, they would aggregate together at step or kink sites of the growing Rh island and could be buried by newly deposited Rh atoms. This is a possible scenario to explain the observed mixing at the interface of Rh-coated Au nanorods [51].

6.2.2 Pd/Au

The second column in Fig. 8 shows MD snapshots for Pd deposition on Au. In contrast to Rh, Pd effectively wets the Au surfaces at this deposition rate, even at low temperatures. This makes it possible for an ideal layer-by-layer growth to take place until the accumulated strain resulting from the lattice mismatch causes some surface reconstructions. If, however, at this point the Pd layer is sufficiently thick the system may be kinetically trapped in a state which is far from equilibrium, where a mixed bulk phase and a surface enriched in Au are expected. This could be a kinetically driven mechanism for the formation of the very sharp Au–Pd interface observed in Fig. 7. It is evident from Fig. 8 that the energy barrier for the interchange of Pd adatoms and surface Au atoms on Au{100} is low enough to

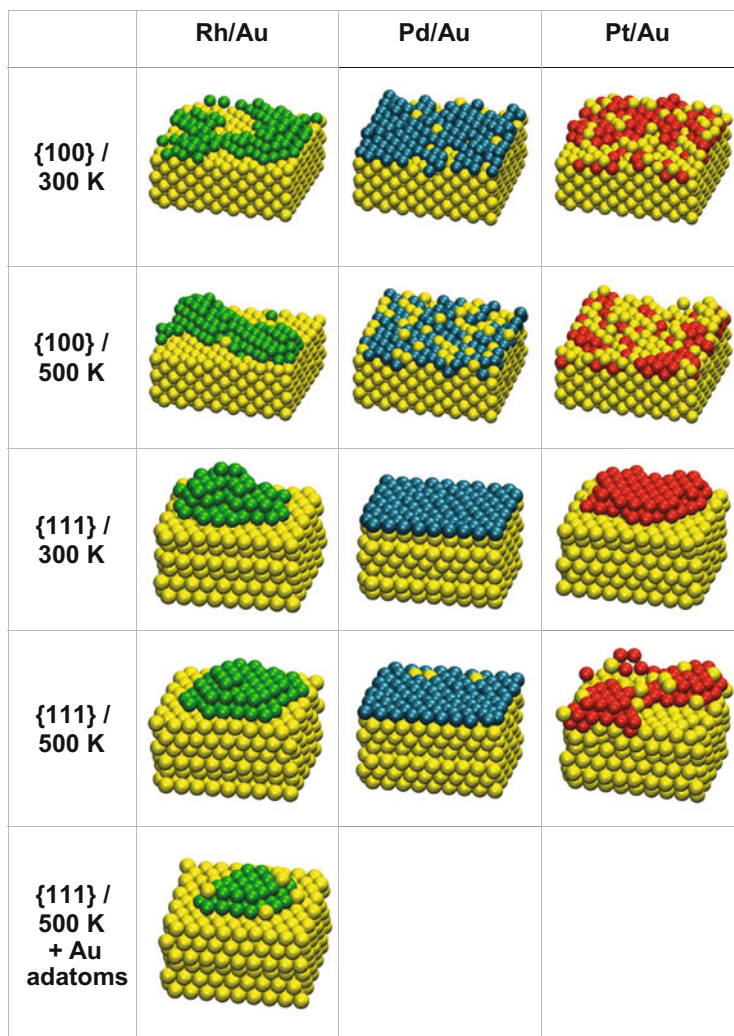


Fig. 8 Snapshots of molecular dynamic computer simulations of Rh, Pd and Pt vapour deposition on Au substrates at temperatures of $T = 300$ K and $T = 500$ K. The deposition rate is at a rate of 1 atom/ns. The *bottom panel* of column 1 is a MD snapshot of a Rh cluster on the Au{111} substrate annealed at 500 K for 20 ns with 8 Au adatoms

occur occasionally even at room temperature. The closer packed Au{111} surface exhibits much greater kinetic stability. In order for mixing at the interface to be prevented, the rate of Pd deposition should be sufficient to form a stabilising wetting layer before any substitutions between the metals can occur. This is consistent with other theoretical calculations conducted for small AuPd clusters, which indicate that increasing shell thickness can improve the stability of segregated structures [68].

6.2.3 Pt/Au

The third column in Fig. 8 shows MD snapshots for Pt deposition on Au. A significantly higher percentage of displacement of {100} surface Au atoms by deposited Pt atoms is observed compared with Pd/Au. Pt and Au, which are mostly immiscible in the bulk, display a greater degree of surface mixing than Pd and Au, which are completely miscible. This situation, which is analogous to that for Rh/Au, can be attributed to the greater difference of the surface energies between the substrate and the deposited element in the case of Pt/Au than in the case of Pd/Au and is consistent with previous simulations by Haftel et al. who modelled the early stages of growth of Pt/Au{100} and Au/Pt{100} surfaces [90]. The apparent mixing in the Pt/Au{100} system is characterised by a certain degree of clustering, although not as pronounced as for Rh/Au. Raising the temperature from 300 to 500 K results in a smoother Pt/Au{100} interface, which is not observed for Rh/Au{100}. Pt deposited onto the Au{111} substrate forms 3D clusters, similarly to Rh/Au{111}, but displays greater wetting of the substrate. Two main differences are evident when comparing the effect of temperature on the Pt/Au{111} and Rh/Au{111} systems. First, there are a greater number of displaced Au surface atoms at 500 K for Pt/Au, which shows that this temperature is sufficient to overcome the energy barrier for this elementary process even on the close-packed {111} surface, which supports the hypothesis put forward for the morphological changes in AuPt nanorods discussed below (Sect. 6.3). Second, the growth at 500 K is characterised by smaller surface clusters than at 300 K. This tendency is opposite to that observed for Rh/Au{100} and results from the very different kinetic picture of the active processes taking place on the surface in both cases. For instance, several Pt atoms implanted in the Au{111} surface at 500 K become nucleation centres, around which 3D surface clusters form, while the geometries of the Rh/Au{100} surface clusters are mainly controlled by the rate of surface diffusion. This also illustrates that the characteristics of surfaces formed by kinetic effects may change in a non-uniform way with temperature, especially in heteroatomic systems such as those considered here.

It should be emphasised that these MD simulations correspond to the physical progress of vapour deposition. They reveal only certain internal properties of the system and tendencies of the deposition process and do not give a comprehensive picture of the growth kinetics, which may be different in the case of chemical deposition. Also, modelling deposition on flat surfaces does not account for the effect of curvature of the nanorod surface, which may result in different strain conditions when the coating film becomes sufficiently thick. Nevertheless, the results from these simulations underline the importance of taking special care in kinetic modelling of such systems to determine the key kinetic processes and to verify whether or not they change within the temperature range under study.

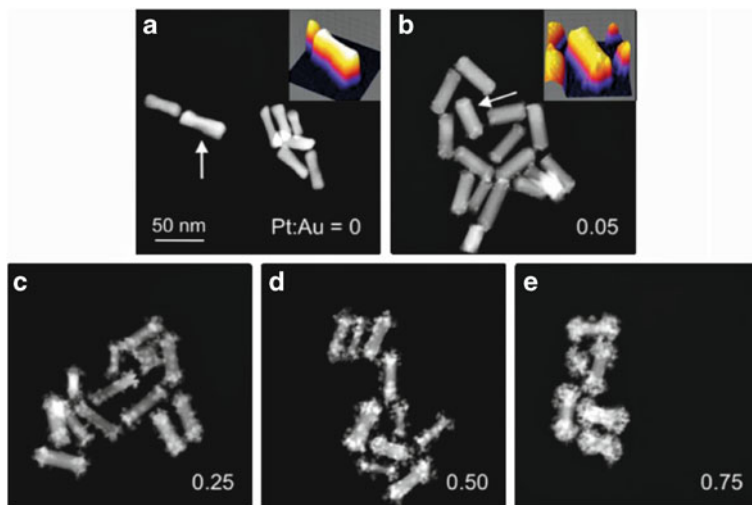


Fig. 9 STEM-HAADF images of AuPt nanorods. (a) Bare Au NR seeds and (b) to (e) Pt-coated Au NRs with Pt:Au ratios, respectively, of 0.05, 0.25, 0.50 and 0.75. The 3D intensity profiles from an as-grown Au NR (arrowed) and a Pt-coated NR (arrowed) are inset in (a) and (b), respectively. Reproduced from [83]. Copyright 2012 American Institute of Physics

6.3 Synthetic Manipulation of Pt on Au Nanorod Growth

As shown in Table 1, the lattice constant of Pt is very similar to that of Pd and its average surface energy lies between those of Rh and Pd. These factors determine similar surface segregation properties at equilibrium as in the AuPd and AuRh systems, namely, that surfaces are expected to be enriched in Au. Pt, like Rh, has a much higher cohesive energy than Au, whereas Pd has a similar cohesive energy. With respect to its miscibility properties in the bulk, the AuPt system is interesting because although Au and Pt are immiscible for most compositions, they form solid solutions in the very Au-rich part of the phase diagram [77]. As a result of this, AuPt can be said to bridge the miscible AuPd system and the more immiscible AuRh system.

Our own study and the work of others conducted on AuPt nanorods indicates a tendency for clustered growth of Pt, with a marked preference for Pt growth on the nanorod end facets [83, 91]; examples from our work are shown in Fig. 9. Growth of Pt (or indeed Rh) on the outside of an Au NR represents a kinetically controlled product rather than the thermodynamically most stable product. Our study has shown that marked changes in the morphology of Pt-coated Au NRs were observed over the course of 18 months when stored under ambient conditions; see Fig. 10 [83]. It seems that, unlike the AuRh and AuPd systems discussed in Sect. 6.1 above, the Au–Pt interface is not stable. Similar morphology changes were observed for AuPt NRs with different amounts of Pt coating. This process can be accelerated by annealing AuPt nanorods at 200°C [83]. It is possible that the mechanism of the

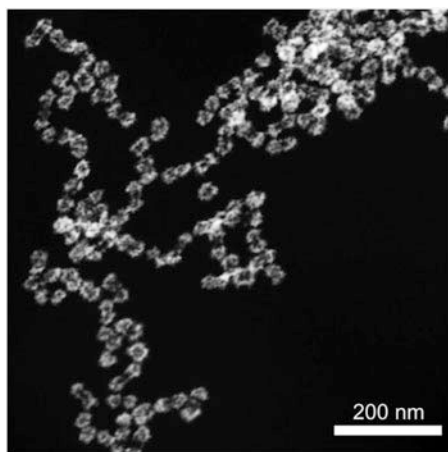


Fig. 10 An overview of the AuPt nanorods showing evolution of morphology. Reproduced from [83]. Copyright 2012 American Institute of Physics

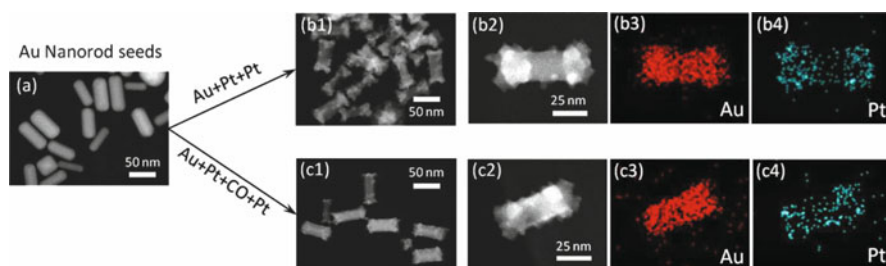


Fig. 11 STEM-HAADF images and EDX elemental maps of AuPt nanorods showing the influence of CO blocking on Pt overgrowth. (a) Bare Au NRs seed, (b1-4) Au–Pt NRs prepared without the CO blocking step, and (c1-4) Au–Pt NRs of same composition prepared with the CO blocking step. Reproduced from [82]. Copyright 2013 American Chemical Society

change in morphology is a result of initial Pt clustering growth that leaves part of the Au surface uncovered especially in the middle of the Au nanorod. The thermodynamic preference for Au-coated Pt probably drives Au to diffuse onto the outside of the Pt, thinning the centre of the NR until it breaks into two nanoparticles. While the AuPt nanorods were kept in solution, the samples were stable, suggesting that the surfactant remaining on the surface may inhibit this diffusion process.

Working on the hypothesis that the incomplete Pt coverage might enable Au diffusion to the outside of $\text{Au}_{\text{core}}\text{Pt}_{\text{shell}}$ NRs, a selective blocking method was developed to even out Pt coverage across the surface of Au NRs. The results from this study are summarised in Fig. 11 [82]. The method involved sequential Pt deposition steps and exploited the difference in binding energies of carbon monoxide (CO) on Au and Pt surfaces. STEM-HAADF, EDX and electrochemical

measurements all indicated that using CO blocking after the first deposition step resulted in the coverage of remaining exposed Au sites with Pt deposited in the subsequent step rather than continued growth at the ends of the NRs. The effect of smoothing Pt deposition and increasing its coverage of Au also resulted in greater stability of the NRs. STEM-HAADF carried out on the same samples after more than 18 months showed that the NRs prepared with CO blocking retained their structure [82].

Our study also showed that the different surface compositions of the Au–Pt NRs prepared with CO blocking and without CO blocking had an influence on catalytic activity and selectivity towards the electrochemical reduction of oxygen. This reaction was more selective towards water as a product and had higher rate constant and specific activity (per area Pt) when carried out with NRs prepared with CO blocking, as a result of the higher Pt:Au surface ratio [82].

7 Conclusions

In this brief review, we have shown the potential to gain a fundamental understanding of, and control over, the atomic detail of metal–metal bonding at the interfaces of core–shell nanorods and nanoparticles. Using a combination of experimental and computer simulation techniques and by making comparisons between related bimetallic systems has proved to be very effective.

Using examples from our recent work, we have shown that experimental structural characterisation can be conducted to great effect by exploiting the atomically resolved capabilities of ac-STEM imaging. For bimetallic nanosystems comprising elements from different rows in the period table (such as AuRh and AuPd), STEM-HAADF imaging can provide elemental information about the interface at the atomic scale. For systems such as AuPt with similar atomic numbers, ac-STEM in combination with EDX elemental mapping provides a very effective method for investigating interfacial structures. The direct visualisation of the interface at the atomic scale highlights the complex range of factors that drive the metal–metal interactions in bimetallic systems and the need for targeted computer simulation of metal-on-metal growth to provide insight into the mechanisms of the observed interfacial structures.

Using molecular dynamic simulations, we have shown the key role played by kinetics in forming the interfacial structures in these AuM systems. Although the complexity of real systems cannot be fully reproduced in computer simulation, this work shows how improved understanding can be achieved through the effective use of computer simulation. [It should be noted that an alternative kinetic Monte Carlo approach could be used to study growth over longer timescales, though this approach is better for fixed-lattice systems and where there is good epitaxy.] Our simulation results have also revealed the potential for kinetic control of synthesis structure during chemical synthesis. Our study using CO blocking during the chemical synthesis of AuPt nanorods has demonstrated experimentally how particle

structure can be controlled at the atomic scale by manipulating kinetics to realise significant reactivity gains.

Research into metal-on-metal growth and the resulting interfacial structures in bimetallic nanoparticles is still rather limited. The nature of interfacial structures impacts directly on reactivity. This review has shown that by taking a combined approach of experimental structural characterisation of interfacial structures, computer simulation of metal-on-metal growth and controlled sample synthesis to manipulate interfacial structure, alongside catalytic reactivity measurements, it is possible to make substantial steps towards the ultimate goal of the rational design of bimetallic nanocatalysts.

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