INTRODUCTION

Metal clusters and nanoparticles

There is still no sharp discrimination between the terms ‘cluster’ and ‘nanoparticle’ in the literature. Clusters are mostly considered as species, exactly defined in chemical composition and structure, whereas the expression ‘nanoparticle’ usually means particles of less precise characterization, often linked with a certain size distribution and so to some extent substitutes the historical expression ‘colloid’. Examples for typical and long-known clusters are \( \text{Co}_4(\text{CO})_{12} \) or \( \text{Rh}_6(\text{CO})_{16} \), exhibiting bridging and terminal CO groups as well as direct metal–metal bonds. Gold nanoparticles (gold colloids), for instance, were already used in ancient times to colour glass (ruby glass) without any scientific understanding. The first who scientifically investigated gold colloid formation was Michael Faraday in the mid-nineteenth century. He reduced a solution of \( \text{HAuCl}_4 \) with elemental phosphorus resulting in the formation of ruby-red gold sols. In the meantime, we learned that the reason for this colour is due to the interaction of visible light with surface electrons of the gold nanoparticles (Mie theory). As we know today, the colour depends on size, shape and surrounding medium. Faraday’s original gold sols contained sub-30nm gold particles with a rather broad size distribution. Nowadays, the number of precise metal clusters and of less precise metal nanoparticles is immense.

From physical and chemical properties, large metal clusters and nanoparticles represent a bridge between the molecular and solid state. As such, they often exhibit properties belonging to both of these classical disciplines and therefore are of immense scientific and practical interest. The aspect that the property of a metallic particle can be designed by the number of atoms is a driving force in modern physics and chemistry. For the size dependence of physical and chemical properties, the expression ‘size quantization’ has been introduced. Clusters or nanoparticles, consisting of metal atoms only, change their physical properties spontaneously from a distinct size on. Metal particles below about 2nm show typical quantum size behaviour, even at room temperature owing to the existence of discrete electronic energy levels and the loss of overlapping electronic bands, the characteristic of a bulk metal. Therefore, they are also called ‘artificial big atoms’ and are to be considered as links between bulk metals and small molecular clusters.

Besides the exciting electronic changes on the way from bulk to molecule or vice versa, other properties change too. For instance, small metal nanoparticles show a significantly lower melting point than the corresponding bulk metal. Magnetic and optical properties also show a typical dependence on the particle size, and the band gap of semiconductor clusters also varies significantly with size.
Many methods for the generation of metal clusters and of metal nanoparticles have been developed since Faraday’s experiments. In principle, two different procedures have become known: top down and bottom up. Top-down syntheses start from bulk metal and apply techniques that destroy the bulk structure by mechanical, thermal or irradiative methods, just to mention a few. Generally, particles of large size distribution result from such methods. In contrast, bottom-up strategies use single atoms or ions to grow clusters and nanoparticles wet chemically of rather precise composition, size and structure. In order to prevent agglomeration, the nanosized entities have to be protected by appropriate ligand molecules serving as a protecting sphere. Bottom-up methods indeed allow under special conditions the generation of identical species. The most important methods are chemical reduction of metal salts and decomposition of preformed organometallics by thermolysis. Besides monometallic species, alloy-like and core–shell particles of two different metals (or even more) also exist, for instance, CoPt$_3$, FePt, PtRu, AuPt, FeNi and numerous others.

Another class of metal-rich clusters and nanoparticles consists of metal atoms, bridged by non-metallic elements, for instance oxygen, sulphur, selenium or phosphorus. Especially for metal chalcogenides, a large number of compounds have become known. They exist with and without protecting ligands. In the bulk state, metal chalcogenides are very often semiconductors. Therefore, reduction in size to the nanoscale yields increasing highest occupied molecular orbital–lowest unoccupied molecular orbital separation. In comparison with metal nanoparticles, the quantum size behaviour develops continuously and not spontaneously.

Of course, it was not possible to consider all different fields and aspects of metal clusters and metal nanoparticles for this Theme Issue of Philosophical Transactions. Some important areas are missing, for instance, the broad class of metal-rich oxometallates and part of main group element clusters. Though the chemistry of oxometallates belongs to the oldest parts of inorganic chemistry, only recently could compounds with hundreds of metal atoms reaching the nano-regime be synthesized and characterized. Clusters of main group metals experience presently a real renaissance. After numerous years of stagnation, today we know molecular clusters of main group elements with up to 84 metal atoms. The interaction of nanoparticles with biosystems (bioresponse) is another not fully considered important new research area with a lot of potential for future applications in medicine. Part of this field is discussed in this issue. From these new developments, one can also see the enormous progress in chemistry, physics and theory. Without high-performance instruments such as high resolution transmission electron microscopy, atomic force microscopy or scanning tunnelling microscopy, this development would never have become possible.

Besides their exceptional scientific attraction, metal-rich clusters and nanoparticles of any type are of increasing practical relevance including in numerous disciplines like physics, chemistry, biology, medicine or material sciences.

The contributions in this Theme Issue have been carefully selected to demonstrate the diversity of this part of modern nanotechnology but, as mentioned above, being aware that in no case could all interesting aspects be considered. There are 12 invited papers discussing the latest research findings in chemistry, physics and theory.
Weigend & Ahlrich’s (2010) contribution focuses on finding the building principles of naked clusters of different types of metals. Besides main group elements (Al, Sn and Mg), the structures of Pd as well as of mixed metal clusters (Ir, Pt) have been calculated with quantum mechanical density functional theory methods. The size-dependent structures of naked cluster cations and anions of Au$_n$ ($n = 3–30$) have been solved by ‘trapped ion electron diffraction’. Schooss et al. (2010) describe this method and the quantum chemical calculations of the structures. Polyanions of group 14 elements are reported in Scharfe & Fässler’s (2010) article. It deals with novel Zintl ions with interstitial heteroatoms such as [Pd$_2$@Sn$_{18}$]$^{14-}$. Simon (2010) describes clusters in the solid state on the basis of suboxides, subnitrides and rare earth elements. Syntheses and structural characterization by X-ray analyses of smaller and nanosized homo/heterometallic Pd clusters are described in the article of Mednikov & Dahl (2010). These species are protected either by CO or PR$_3$ ligands. Three contributions are related to nanosized metal and semiconductor particles. Sperling & Parak’s (2010) contribution reviews strategies of modification and functionalization of gold and CdSe/ZnS species. Bigall & Eychmüller (2010) present the synthesis of noble metal nanoparticles and their superstructures. Additionally, methods for fabricating non-ordered large surface materials of gold, silver and palladium are presented. Homberger & Simon’s (2010) article not only deals with the electronic situation of gold clusters and nanoparticles with respect to future applications in nanodevices, but also with the interaction of selected gold systems with biomolecules. The transition from innocent bulk gold to highly cell-toxic nanoparticles is of promising relevance (see cover picture). MacDonald & Corrigan (2010) discuss a new method for the preparation of ligand stabilized nanometre-sized Cu and Ag chalcogenide clusters. The structures of these compounds have all been solved by single crystal X-ray diffraction studies. Two papers present species with application potential. Adams & Trufan (2010) summarize syntheses and characterization of Ru–Sn clusters as precursors for heterogeneous catalysts, whereas Corain et al. (2010) deal with systems consisting of cross-linked functional polymers containing various metal nanoparticles. Transition metal clusters and networks with interesting magnetic properties are the focus of the article of Kostakis et al. (2010).

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References


