Chapter 1

Introductory Chapter: Overview of the Properties and Applications of Noble and Precious Metals

Mohindar S. Seehra and Alan D. Bristow

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http://dx.doi.org/10.5772/intechopen.75503

1. Introduction

The noble and precious metals correspond to a selection of the transition-metal group of the periodic table (see **Figure 1**), including copper (Cu), silver (Ag), gold (Au), platinum (Pt), palladium (Pd), iridium (Ir), osmium (Os), ruthenium (Ru), rhodium (Rh), and rhenium (Re). Pt also gives its name to a distinct subset of these elements, known as the platinum group, which include Ru, Rh, Pd, Os, Ir, and of course Pt. Additionally, Ru, Rh, Re, Os, and Ir are considered refractory metals—defined by melting points exceeding about 2000°C—along with several more abundant and commonly used transition metals, such as titanium (Ti), chromium (Cr), molybdenum (Mo), and tungsten (W). The noble and precious metals generally crystallize in the face-centered cubic (fcc) structure except for Ru, Re, and Os, which have the hexagonal close-packed (hcp) structure. The use of Cu, Ag, Au, and Pt in jewelry and coinage has been known throughout human history. The chapters presented in this book deal with other applications of some of these metals along with their fundamental properties.

This introductory chapter presents a survey of important properties and applications of noble and precious metals. These include properties at the nanoscale and their applications, particularly in the areas of catalysis and biomedicine. Only a brief mention of these properties is made, giving references to recent papers and reviews, which the readers can utilize to gain access to more comprehensive literature on the subject. The chapter is organized in sections with each section devoted to a single noble and precious metal.

Platinum Group Other Precious Metals				29 **Copper** (Cu)
	44 **Ruthenium** (Ru)	45 **Rhodium** (Rh)	46 **Palladium** (Pd)	47 **Silver** (Ag)
75 **Rhenium** (Re)	76 **Osmium** (Os)	77 **Irridium** (Ir)	78 **Platinum** (Pt)	79 **Gold** (Au)

Figure 1. Section of the periodic table corresponding to precious and noble metals, depicting atomic number chemical name and symbol.

2. Copper (Cu)

Being the most abundant and least expensive of the noble and precious metals, with excellent electrical and thermal conductivity, copper is used extensively in electrical power transmission, plumbing, cookware, etc. However, because of the reactivity of Cu toward oxygen, water, and other chemicals, synthesis of Cu nanoparticles (NPs) requires special procedures [1]. The synthesis and applications of Cu and Cu-based nanoparticles (NPs) to catalysis including gas-phase catalysis, electro-catalysis, and photocatalysis are reviewed by Gawande et al. [1]. The review paper by Din et al. [2] has described various methods for the synthesis of Cu NPs including chemical, physical, and biological methods. Medical applications of Cu NPs include their use as antibiotic, antifungal, and antimicrobial agents.

3. Silver (Ag)

The important properties of silver include its good electrical conductivity and its chemical stability. Bulk Ag is a common material for high-quality reflectors of electromagnetic radiation in the visible regime, superseding cheaper non-noble metals such as aluminum. On the nanoscale, Ag-NP applications include their catalytic activity and antimicrobial properties such as improving the microbial quality of drinking water [3]. Various methods for synthesizing Ag-NPs are described in the recent paper of Alaqad and Saleh [3]. Synthesis of metallic nanoparticles of Ag, Au, Pt, and Pd employing plant extracts is reviewed in the recent paper by Akhtar et al. [4]. Other review papers on the synthesis, applications, and toxicology of Ag-NPs are those by Iravani et al. [5] and Tran et al. [6]. Finally, Jo et al. [7] have reported ferromagnetism in Ag-NPs and associated it with the surface atoms on the Ag-NPs whose percentage concentration increases with decrease in particle size. In addition to extensive NP fabrication, nanoscale films of Ag have been grown using molecular beam epitaxy to improve the underdeveloped area of plasmonics [8], where optical excitation leads to a collective oscillation of electronic plasma in the metal.

http://dx.doi.org/10.5772/intechopen.75503

4. Gold (Au)

Historically, accumulation of gold by people and nations has marked their economic wealth. Because of exceptional chemical stability and good electrical conductivity, gold is a good scientific material for contacts. Au is one of the best optical reflectors throughout the infrared region of the electromagnetic spectrum. Like many of the noble metals discussed here, its optical and dielectric constants can be found in both Johnson and Christy [9] and Palik [10].

Au-NPs exhibit a strong size-dependent position of a localized plasmon resonance and attracted considerable attention in recent years in technologies such as biomedicine (diagnosis, imaging, sensing), catalysis, and electronics. The review paper by Daniel and Astruc [11] and follow-up papers by Jain et al. [12], Huang et al. [13], and Piella et al. [14] are good sources for accessing literature on Au-NPs and their many applications. Another interesting aspect of Au-NPs is their size-dependent magnetic properties which are believed to originate from electron transfer between surface atoms of Au and capping agent (thiols) [15, 16]. The strength of ferromagnetic moment originating from this electron exchange at the surface varies as 1/D where D is the size of the particles. Furthermore, Au-NPs can be readily coated with dielectric materials to protect the metal from erosion due to photocatalyzing chemical reactions and provide a wider range of absorption energies for solar light harvesting [17].

5. Platinum (Pt)

Platinum is less abundant than Cu, Au, or Ag but has a similar place in history as the latter two as a material of value. Like the other metals, it is ductile and malleable but denser and harder to work. Pt is remarkably chemical unreactive, but as the electronic structure calculations of Andersen for Pt, Pd, Ir, and Rh show [18], Pt has a large free electron density, making it a good chemical catalyst. Pt is widely used in catalytic converters to oxidize carbon monoxide produced in internal combustion engines [19]. Pt is also used as contacts in situations that exploit the chemical stability, for example, at extreme temperatures or in salt water conditions [20]. It is also a versatile electrode in electrochemical experiments [21].

At the nanoscale, Pt NPs have also been engineered, primarily for catalytic applications [22]. Other potential applications of Pt NPs reported in literature are in cancer therapy [23, 24]. For size <5 nm of Pt NPs, observations of superparamagnetism [25] and ferromagnetism [26] have been reported.

6. Palladium (Pd)

Pd is a silvery white metal, and it is often found in deposits along with Pt as well as deposits of Ni and Cu. Pd is resistant to corrosion, and its alloys are used in jewelry as "white gold."

One of the distinguishing properties of Pd is its enormous capacity to absorb hydrogen in the ratio of about 900:1 by volume, making it an excellent catalyst for hydrogenation and dehydrogenation reaction [27]. The absorption of H_2 leads to the reversible formation of PdH_x.

Several groups have reported the synthesis of Pd NPs by different techniques [28, 29] and their various applications such as antimicrobial agents [30, 31] and for surface-enhanced Raman scattering [32, 33]. Regarding its magnetic properties, development of a ferromagnetic moment with decrease in particle size of Pd to nanoscale sizes has been reported by several groups and interpreted on a core-shell model [34–37]. In this model, atoms in the core retain the properties of bulk Pd, whereas atoms in the shell develop a ferromagnetic feature due to reduced symmetry of the surface atoms and electron exchange with the capping agents.

7. Iridium (Ir)

Iridium is a silvery white metal with high resistance to corrosion, and it is very dense (density = 22.55 gm/cm^3). In Earth's crust, it is quite rare, about two parts per billion (ppb), and often found with other noble metals. As a metal, it is unworkable but finds use in space components and specialty spark plugs when alloyed with Pt. In recent years, nanoparticles of Ir have been synthesized using various chemical techniques [38, 39] and tested as catalysts [40–42] and as sensors [43–45]. Examples of catalytic activity are the use of Ir NPs for the degradation of dyes [38] and for hydrogenation reactions [41, 42]. As biosensors, Ir NPs have been tested for the detection of glucose [43, 44].

8. Osmium (Os)

Osmium is a member of platinum (Pt) group, and it is often found in ores of Pt. Like Ir, it is also very rare in Earth's crust (~1 ppb) and has very high density (22.58 gm/cm^3) and high melting point (~ 3000°C). Although Os is an unworkable metal, Os-Pt alloys are harder than Pt and are often used in specialty equipment. Its oxide, OsO_4, is quite toxic to the respiratory system.

In recent years, there have been several reports on the synthesis of nanoparticles of Os [46–47] and Os alloys for potential applications. Applications reported so far include the following: use of Ni-Ir and Ni-Os bimetallic NP alloys for hydrogenation reactions [48], Os NPs for CO oxidation [49, 50], and Os NP electro-catalysts for PEM fuel cells [51] and direct methanol fuel cells [52].

9. Ruthenium (Ru)

Ruthenium is normally found as a minor component of Pt ores, is chemically inert, and has a silvery color. Ru has the electron configuration of a $5s^1$ outer shell, making it more like Rh, Au, and Pt than the rest of its own group [iron (Fe), Os, and hassium (Hs)] which have an s^2

http://dx.doi.org/10.5772/intechopen.75503

outer shell. In many respects Ru differs from Fe, except in the aqueous cations it can form. It marks a point in the periodic table that distinguishes the second and third rows, as well as the left and right sides of the block of transition metals.

At the level of less than 1% concentration, Ru can increase the hardness of Pt and Pd alloys, can markedly increase the corrosion resistance of titanium (Ti), [53] and is found in superalloys that operate in extreme high temperatures, such as in jet engine turbines [54]. Of course, like most noble and precious metals, Ru is a contact material that has comparable properties to Rh alloys achieved at a lower cost [54]. In particular, Ru can be found in dimensionally stable anodes and optode sensors operating in corrosive environments. Moreover, ReO_2 and $MReO_3$ (where M is a metal) compounds appear in electronics as thick-film resistors [55]. Other ruthenates appear in explorations of superconductivity, magnetism, and multiferroic prototypes. Although bulk Ru is a paramagnet at room temperature and when alloyed with molybdenum, it becomes a superconductor below 10.6 K [56]. Organometallic NPs and carbon-supported NPs containing Ru have been synthesized for application related to solar cells [57] and catalysis [58, 59]. There is a wide range of work on Ru in both homogeneous and heterogeneous catalyses and the synthesis of Ru NPs [47, 49, 50].

10. Rhodium (Rh)

Rhodium is hard, silvery-white transition metal that is both corrosion resistant and chemically inert. Rh is one of the rarest elements to be found on Earth, which slowed its uptake as anything other than a precious metal used for decoration in white-gold jewelry. Rh is now in common use, since the invention and legal requirement for three-way catalytic converters to reduce NO_x produced in the exhaust of combustion engines [54]. Hence, the predominant use of Rh is in the automotive industry. There have been other applications, such as early-generation Rh-based neutron flux detectors and electrical contacts where economics meet the small electrical resistance requirements. Current alternative uses include coatings for optical instruments [60] and catalysis in biological applications [61–63]. Heterogeneous catalysis has also been advanced by the fabrication and use of bimetallic Rh-based core-shell nanoparticles [64]. Ferromagnetism in Rh NPs has been reported in Ref. [35].

Depending on how the automotive and other industries progress in the next few decades, new or recycled sources of Rh may be required. Recycling from electronic and catalytic industries seems promising. Alternatively, because Rh is a by-product of uranium-235 fission, reclamation from nuclear fuel waste may become commercially viable.

11. Rhenium (Re)

Rhenium has a melting point that is exceeded only by W and carbon (C). It is dense metal with a white-silver hue. Unlike many of the other noble metals, Re is more commonly extracted along with Mo than with Pt; hence, it is not part of the platinum group. Nonetheless, it has similar corrosion-resistant, high-temperature alloying advantages of much of that group. Once again, major applications are in extreme conditions Examples include Pt-Re alloys used for refining lead-free high-octane fuels where its inert properties avoid chemical degradation [65, 66] or W-Re and nickel-Re superalloys that withstand high temperatures as jet engine coatings [67]. W-Re alloys are more ductile at low temperature and more stable at high temperature, properties which also allow them to withstand electron impacts during the generation of X-rays and acting at thermocouples for extreme temperatures. In more recent years, metal–organic NPs containing Re has been explored for use in biological application [61] and to enhance catalysts [68]. The synthesis of Re NPs has been reported by Ayvali et al. [69] and Kundu et al. [70], the latter authors also reporting the applications of Re NPs in catalysis and surface-enhanced Raman scattering. Also, Re dichalcogenide films have been grown to study their electronic, optronic, and spintronic properties [71], extending the family of van der Waals-bonded transition-metal dichalcogenide which offer layer-by-layer tailoring of device properties.

12. Concluding remarks

As described above, noble and precious metals play essential roles in a wide range of technologies. Development of new coating materials, contacts, emitters, and catalysts is essential to better performances in engines, synfuels, and electrical components alike. Not only is material fabrication, especially at the nanoscale, an ongoing and vital area of research and development, so is the extraction, refining, and reclamation. One such example is the growing industry of metal recovery from the vast output of old products produced by the consumer electronic market. Similarly, transition-metal compounds are routinely at the center of new breakthroughs in fundamental physics that may one day lead to unthought of technologies. Regardless of the direction, the investigations into the properties and applications of these metals remains active, with more developments expected in the future.

Author details

Mohindar S. Seehra* and Alan D. Bristow

*Address all correspondence to: mohindar.seehra@mail.wvu.edu

Department of Physics and Astronomy, West Virginia University, Morgantown, WV, USA

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