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Supported transition metal nanomaterials: Nanocomposites synthesized by ionizing radiation

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ABSTRACT

Nanostructures decorated with transition metal nanoparticles using ionizing radiation as a synthesis method in aqueous solutions represents a clean alternative to existing physical, chemical and physicochemical methods. Gamma irradiation of aqueous solutions generates free radicals, both oxidizing and reducing species, all distributed homogeneously. The presence of oxidant scavengers in situ during irradiation generates a highly reductive environment favoring the reduction of the metal precursors promoting seed formation and nanoparticle growth. Particle growth is controlled by addition of surfactants, polymers or various substrates, otherwise referred to as supports, which enhance the formation of well dispersed nanoparticles. Furthermore, the combination of nanoparticles with supports can offer desirable synergisms not solely presented by the substrate or nanoparticles. Thus, supported nanoparticles offer a huge diversity of applications. Among the ionizing radiation methods to synthesize nanomaterials and modify their characteristics, gamma irradiation is of growing interest and it has shown tremendous potential in morphological control and distribution of particle size by judiciously varying parameters including absorbed dose, dose rate, concentration of metal precursor, and stabilizing agents. In this work, major advances on the synthesis of supported nanoparticles through gamma irradiation are reviewed as well as the opportunities to develop and exploit new composites using gamma-rays and other accessible ionizing radiation sources such as X-rays.

1. Introduction

Transition metals at the nanoscale have shown a unique combination of physical and chemical properties which offer a wide range of possible applications in diverse fields such as information storage, optoelectronics, sensors, fuel cell technology and catalysis among others (Campelo et al., 2009; Cuenya, 2010; Datsyuk et al., 2008; Du et al., 2015; Kawasaki, 2013; Kuila et al., 2012; Marquardt et al., 2011; Okitsu et al., 2000; Wildgoose et al., 2006; Xu et al., 2008). Supports are often used for the synthesis of nanoparticles since they provide improved distributions onto the surface which helps to prevent aggregation (Barros et al., 2012). It is known that nanoparticles are prone to aggregation in order to reduce their surface energy as a result of their relatively high surface area which causes deleterious effects in their physical and chemical properties negatively impacting performance. Thus, the selection and use of adequate supports during the synthesis helps to stabilize the nanoparticles and prevent further aggregation while maintaining their characteristics (Campelo et al., 2009). Traditional nanoparticle synthesis methods include co-precipitation, impregnation and deposition-precipitation while other more environmentally benign synthesis methods involve microemulsions, photochemical or electrochemical reductions. The latter approaches are sometimes referred to as *green chemical methods*. Some technologies such as sonochemistry, microwaves, laser, sonication, and plasma, have been developed aiming to satisfy requirements of an *ideal nanomaterial synthesis*: controllability of size/shape, scalability, minimal steps to follow, precursors having low toxicity, non-toxic solvents, low reaction by-product formation, low hazardous waste generation, and few chemical reagents. For instance, in sonochemistry, reduction and deposition occurs consecutively, heating is not required, and the particle size can be controlled (Kawasaki, 2013).

Nowadays, there is an increasing interest in research towards revolutionary synthesis methods that have potential for producing uniform, high quality nanomaterials while maintaining feasibility, scalability, and reproducibility. Special attention is given to those methods whose implementation of the manufacturing process is considerably easier than current ones. For example, methods that do not require the use of harsh chemicals and high temperatures or pressures are desirable. On this effort, radiation chemistry has significantly contributed to the progress in this area (Gerasimov,

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2011; Kharisov, 2013; Ohkubo et al., 2014; Remita et al., 2007; Rojas et al., 2015, 2016; Zhang et al., 2010b). The interaction of ionizing radiation, such as gamma rays and X-rays, with aqueous solutions leads to generation of randomly distributed reducing and oxidizing agents with large redox potentials. Through the use of scavengers, e.g. 2° and less often 1° alcohols, the environment in the solution can be modified to generate a high concentration of reducing agents. These species can readily react with solvated metal ions and decrease their oxidation state (Belloni et al., 1998; Remita et al., 2007). Subsequently, the metallic atoms obtained in solution nucleate into clusters and grow into particles. This synthesis method is environmentally benign in part due to elimination of harsh chemical reducing agents which may also poison the nanomaterial and affect their behavior. Moreover, the synthesis is carried out under desirable conditions for a large number of applications (i.e. catalysis, drug delivery) such as aqueous environments under ambient temperature and pressure. Gamma irradiation is a mature technology and has been widely used in various fields ranging from the pharmaceutical industry to materials engineering. This technique represents a revolutionary and clean approach to the controlled synthesis of nanomaterials.

It is important to highlight safety considerations when working with gamma sources in any experimental procedure. Researchers working with ionizing radiation as in the case of synthesis will likely work with gamma irradiators that are equipped with robust shielding features and rely on Co-60 as an emitter (energies ≈ > 1 MeV). These shielding features are designed to prevent any direct human exposure to the radioactive source preventing user tampering and direct manipulation. Furthermore, these shielding features include appropriate safety interlocks which are designed and integrated in a manner to where they cannot be by-passed or overridden by a user. In general, the higher the energy of the radioactive source, the thickness of the shielding must increase and higher atomic mass (Z) elements such as Pb offer excellent radiation shielding characteristics.

2. Radiation chemistry of metal colloids

2.1. Radiolysis of water

The process of radiolysis of water, which result from the interaction of ionizing radiation with matter, has been a subject of substantial investigation as it plays an important role in a wide variety of applications in nuclear science and technology. In order to ionize water, an energy of 13 eV is needed, and if this energy requirement is met, ions, electrons, and extremely unstable radicals are generated where some have very low half-lives (~ 10^{-10} s) (Tubiana, 1990). Among the formed intermediate products, which are discussed in further detail, are hydroxyl radicals, OH•, and more importantly, for synthesis application, electrons. These electrons, also referred to as solvated or electrons in aqueous solution (e_{aq}^-), possess reductive properties as they have a very negative reduction potential of E_o=−2.87 V while the OH• possess the strongest oxidative properties with an oxidation potential of E_o=+2.73 V. Belloni et al. (1998) and Kharisov (2013) Moreover, electrons have initial kinetic energies that allow travel only up to approximately 15 nm because they lose energy by collisions and are eventually captured by highly polarized molecules of water.

During radiolysis of water a number of other reactions occur leading to a gamut of other species which include: H•, H_3O^+, $O^{\bullet}_2^-$ H_2O_2, and H_2. For purpose of comparison, the G factor provides the concentration of species created in this process which is defined in units of μmol/J, or concentration of species per (radiation) energy absorbed. The G factor, or intermediate product yield, depends of the linear energy transfer (LET) of the radiation, pH and purity of the water. The values are summarized in Table 1 for several radiolytically formed species (Belloni, 2006; Tubiana, 1990).

Table 1
Radical and molecular product yield in for various LET of the particles (Tubiana, 1990).

LET	G factor (μmol/J)				
(*keV* μm^{-1})	e_{aq}^-	OH•	H•	H_2	H_2O_2
0.23	0.273	0.283	0.057	0.047	0.070
12.3	0.153	0.185	0.064	0.070	0.087
61	0.075	0.094	0.044	0.100	0.104
108	0.044	0.056	0.028	0.115	0.112

2.2. Radiation synthesis of metal clusters

As mentioned in Section 2.1, the species formed during radiolysis of water include H•, e_{aq}^-, and OH• and are all very reactive where the first two have negative reduction potentials of E° (H$^+$/ H•) =−2.3$_{VNHE}$, and E° (H_2O/e^-_{aq}) =−2.87$_{VNHE}$, respectively. They can each reduce solvated metal ions to zero-valence as shown by Eqs. (1) and (2), where M^+ are monovalent metal ions (Belloni, 2006).

$$M^+ + e_{aq}^- \rightarrow M^0 \quad (1)$$

$$M^+ + H^{\bullet} \rightarrow M^0 + H^+ \quad (2)$$

On the contrary, hydroxyl radicals (OH•), would bring the ions or the atoms to a higher oxidation state. In order to combat this issue, additives such as secondary alcohols or formate anions, ($HCOO^-$), are used as OH• radical scavengers, and, as a result, more reducing species are generated and a highly reducing environment is promoted. The need for additional chemicals, or reducing agents, are eliminated with use of ionizing radiation (eg. γ, β) for the reduction of metal ions; when compared with other reduction methods, excess reagents are typically required in order to reduce metal precursors (Belloni, 2006; Belloni and Mostafavi, 2008; Belloni et al., 1998).

The scheme in Fig. 1 depicts the process of supported metal (M) nanoparticle synthesis via irradiation by ionizing radiation sources. Initially, the reducing agents generated during radiolysis of water, such aqueous electrons, reduce the ions to a zero valence state and this can be a rather complex process where the ions are reduced to intermediate valence states. Once the atoms are uniformly generated in the solution, they tend to dimerize (M_2) or interact with ionic species forming

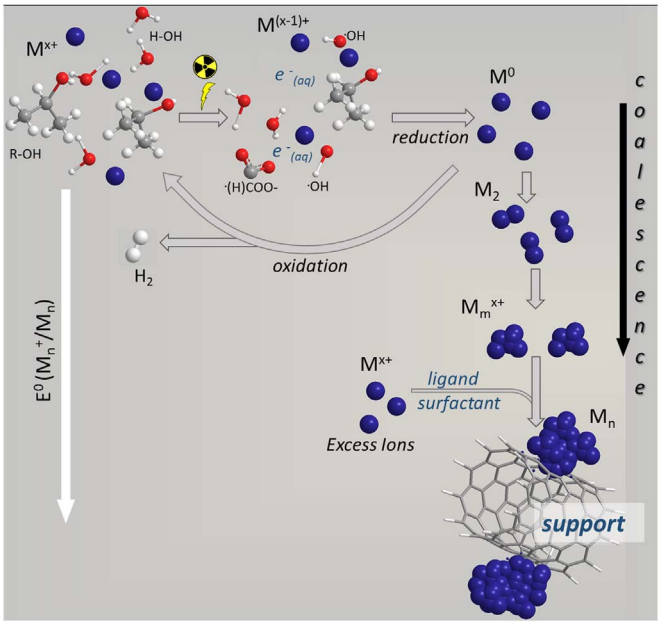

Fig. 1. Metal nanoparticle on support formation under irradiation by ionizing radiation. Original image, adapted from (Belloni, 2006).