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Concepts for the Stabilization of Metal Nanoparticles in Ionic Liquids

Alexander Kraynov and Thomas E. Müller
CAT Catalytic Center, ITMC, RWTH Aachen University
Germany

1. Introduction

Nanoparticles - assemblies of hundreds to thousands of atoms and a size in the range of 1-50 nm - can be considered at first approximation as a state of matter intermediate between single atoms or molecules and bulk bodies. While the properties of atoms and molecules can be described *via* quantum mechanics, the properties of bulk bodies are described by solid-state physics. Using quantum chemical models for describing nanoparticles is demanding because of the huge number of strongly interacting atoms, which have to be taken into account. On the other hand, methods of solid state physics cannot always be applied as nanoparticles often demonstrate size dependent quantum effects,[1] *e.g.*, in surface plasmon resonance.[2, 3] Magnetic,[4] thermodynamic,[5] catalytic [6] and other properties of nanoparticles can also depend on their size.

Due to their small size, nanoparticles have a very high specific surface area and dispersion, the latter being defined as the ratio of the number of surface atoms to the total number of atoms in the particle. Platinum particles with 2 nm diameter, *e.g.*, have a surface area of 140 m2/g and a dispersion of 50 %. Note that also the relative concentration of atoms located at corners, edges, and faces is strongly size dependent (Fig. 1).[7] These surface atoms are not equivalent to each other and frequently play different roles in catalysis. In the following, we focus on metal nanoparticles,[8-10] as one can find good reviews about metal oxide [11-16] and semiconductor [17-23] nanoparticles elsewhere.

One of the most attractive features of unsupported metal nanoparticles is the possibility to apply physicochemical methods to investigate them and to catalyze chemical reactions by exactly the same material. Thus, unsupported metal nanoparticles are frequently used as a model system for conventional heterogeneous catalysts as many physicochemical methods cannot be applied directly to conventional catalysts due to their heterogeneous nature, interfering support effects, and low transparency for electromagnetic radiation. In other words, nanoparticles can serve as models for ideal surfaces and are good candidates to fill the so-called pressure material gap.[24, 25]

It is of great interest to study nanoparticles in ionic liquids, primarily for applications in electrochemistry and catalysis, as they display advantages in comparison to polymer stabilized nanoparticles. These advantages lie, *e.g.*, in the stabilization mechanism, the relative ease of adjusting the properties of the nanoparticle-ionic liquid system, as well as aspects associated with green chemistry. The applicability of nanoparticle suspensions

depends on the strategy employed for stabilization (*vide infra*), which determines how strongly the nanoparticles are stabilized against agglomeration. In the following, we will focus on the use of ionic liquids as a unique medium and highly effective stabilizer. We will describe the concepts of electrostatic, steric, and diffusional stability of nanoparticles as well as discuss the different preparation strategies for metal nanoparticles in ionic liquids. Although we will describe the boundary conditions for the design of the nanoparticle-ionic liquid system for catalytic applications, we will not discuss the use of nanoparticles as a catalyst for specific reactions.
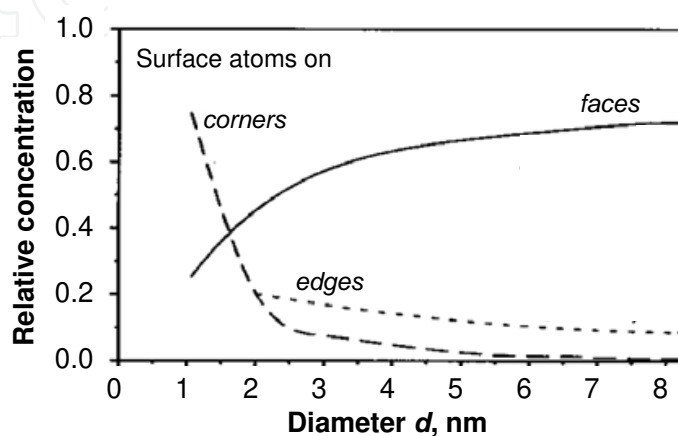

Fig. 1. The relative concentration of the different types of surface atoms n^S_i/n^S in dependence of the size of, here, a silver nanoparticle.[7]

2. Stabilization of metal nanoparticles

Dealing with phenomena associated with surfaces, it is useful to specify the term "clean surface". Atomically clean metal surfaces can be made and maintained only under ultra high vacuum, but do not exist in a chemical flask. As soon as the surface gets into contact with matter, it adsorbs it (as this process generally results in a decrease of the total energy of the interface), even when this material is an inert gas or an alkane. The adsorption mode (physi- or chemisorption) determines how strong the interaction is. Generally, we call adsorption to be strong, when the adsorption energy ΔG_{ads} is higher than ~ 30-40 kJ/mol. This implies that the probability that the sorbate desorbs from the surface at room temperature is very small (RT = 2.48 kJ/mol at 298 K). The residence time τ_a, the time passed between adsorption of a sorbate molecule and subsequent desorption from the surface, is an exponential function $\tau_a = \tau_0 \cdot e^{\Delta G_{ads}/RT}$ of the adsorption energy ΔG_{ads} and the reverse of the temperature T, where τ_0 is the characteristic time of surface atom vibrations (typically 10^{-12} 1/s).[26] The residence time quickly decreases with increasing temperature. At a given temperature, the residence time can be decreased, when the system (sorbate on surface) is exposed to an external influence, such as an external electric field, *e.g.*, induced by the presence of polar solvent molecules (*vide supra*). In further, we call a surface to be clean, when no molecules are strongly adsorbed, while it may be covered with weakly interacting molecules (molecules of dissolved gas, alkanes, *etc.*).

Nanoparticles have a particular tendency to lower their very high surface energy, which is the origin of their thermodynamic instability. Bare nanoparticles tend to stabilise themselves either by sorption of molecules from the surroundings or by lowering the surface area

through coagulation and agglomeration. In order to avoid the later, nanoparticles have to be (kinetically [26]) stabilized. The three conceptions of *electrostatic*, *steric*, and their combination *electrosteric* repulsive forces are generally discussed in literature and are summarized below. The concept of stabilising nanoparticles in viscous media, where the diffusion constants are low, will be introduced new.

2.1 Electrostatic stabilization

The origin of electrostatic stabilization is the repulsive electrostatic force, which nanoparticles experience, when they are surrounded by a double layer of electric charges. The Derjaguin, Landau, Verwey and Overbeek (DLVO) theory [27, 28] considers initially charged colloidal particles whereby the electric charges are uniformly distributed over their surface. The total energy potential V_T of the interaction between two particles is then described as the sum of attractive (van der Waals) contributions and repulsive forces (due to a double layer of counter ions). The height of the overall potential barrier V_T determines, whether the particles are stable (the kinetic energy E_k of particle motion is less than V_T) or not ($E_k > V_T$). The average kinetic energy is defined through the quadratic mean velocity or temperature of the system according to formula (1).

$$E_k = \frac{m<V^2>}{2} = \frac{3}{2}kT \qquad (1)$$

One of the central parts of the DLVO theory is the quantitative prediction of particle coagulation, when electrolytes are added to the system.[29] The formation of virtual charges, however, is neglected. Later is important for conducting (metal) spheres in contrast to non-conducting (metal oxide) spheres. Further, the stability or instability of metal nanoparticles cannot be described based on electrostatic stabilization only.[30] To the best of our knowledge, there is no example in the literature, where colloidal metal nanoparticles are stabilized over an extended period of time only by charges induced by the presence of small ions. This instability is probably a consequence of the very high specific surface energy of metal surfaces (1000-2000 mJ/m²) [31-35] in comparison with other organic and inorganic materials (~20 mJ/m² for teflon and 462 mJ/m² for silica) [36] as well as additional attractive dipole-dipole interactions between the metal nanoparticles.

Charge polarization of two interacting metal spheres as origin of virtual charges was included by Levine and Dube in 1940.[37] They postulated that the interaction energy results from the undistorted penetration of the double layers as well as induced dipole and quadrupole moments. Extending this description to metal nanoparticles requires exhaustive mathematical treatment even in the approximation of classic electrostatic theory, which is well beyond the scope of this chapter. Below, we will introduce a simple, well established model,[38, 39] where the redistribution of electron density within the metal nanoparticle is taken into account. The resulting electric multipoles determine the strength of the electrostatic interaction between the nanoparticles and, thus, their stability.

Let us consider now, how a neutral metal particle interacts with one or several approaching ions assuming that chemical interactions are absent and then investigate how this single particle interacts with another similar particle.

It is generally assumed that the approach of negatively charged anions (rather than positive cations) to a metal sphere induces a partial positive charge (δ^+) on the surface (Table 1 A).[40]
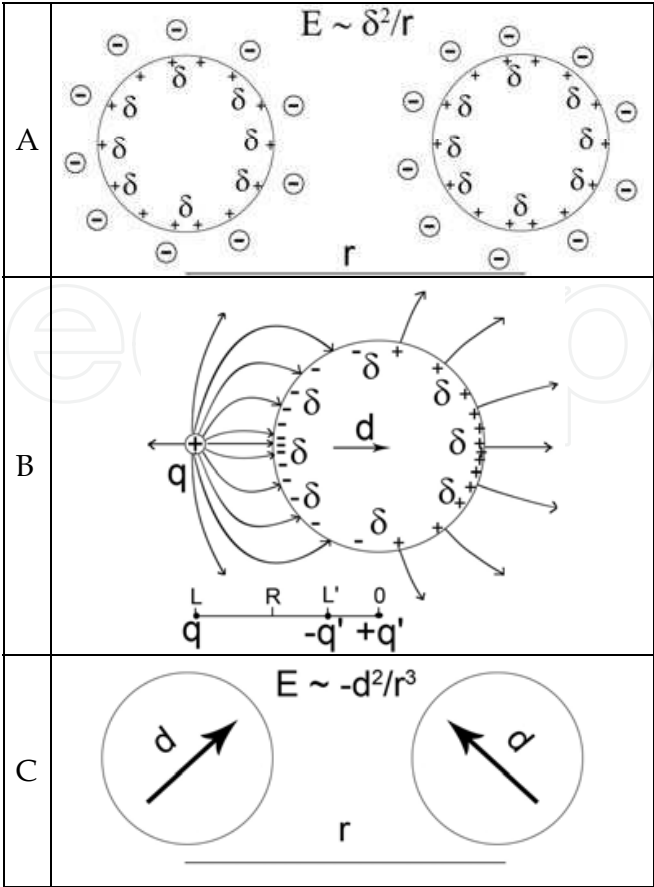
Table 1. *A* – Coulomb repulsion between partly charged particles as the origin of electrostatic stabilization. *B* – Distribution of the surface charge and geometry of the electric field of the neutral metal sphere of radius *R* , when the adsorbate is a single external charge *q* in the distance *L* from the centre. The electric potential of this system is equivalent to the superposition of the potential of an external point charge *q* and the induced dipole moment *d*. *C* – Attractive dipole-dipole interaction between electrically neutral metal particles.

Equally "charged" particles repel each other, which is the basis of general electrostatic stabilization.[30, 40] However, this description does not fully consider that the electron charge density on the metal sphere is redistributed. Let us assume that an external charge *q* approaches the surface of a neutral non-grounded metal sphere (Table 1 B). Note that this implies that the overall electric charge of this sphere is zero and remains so. Close to the approaching charge, an excess of surface charges (with opposite sign) accumulates, whereas excess charges of opposite sign appear on the other side of the sphere.[38, 39] Table 1 B illustrates schematically the induced surface charge and the geometry of the electric field. Based on classic electrostatic theory, it can be shown that the total electrostatic potential (and electric field) is a superposition of the potential of the external charge *q* and an induced dipole moment *d* (Eq. 2), where q' and $-q'$ are virtual charges located in the centre and at a distance L' from the centre of the sphere). The interaction energy (*E*) between the external charge *q* and the metal sphere is half of the sum of the interaction energy between the charge pairs *q*, $-q'$ and *q*, $+q'$ (Eq. 3). Since the second term is larger than the first, the total interaction energy is negative, thus, resulting in an attractive force.

$$d = -q^{'}L^{'} = qR^3 / L^2 \text{ , where } q^{'} = -\frac{R}{L}q \text{ , } -q^{'} = \frac{R}{L}q \text{ , } L^{'} = \frac{R^2}{L} \tag{2}$$

$$E = \frac{qq^{'}}{2}(\frac{1}{L} - \frac{1}{L - L^{'}}) \tag{3}$$

It is important to note that the metal particle stays electrically neutral (rather than partly charged), carrying an electric dipole moment. The later is a function of the magnitude of the external charge q, its distance (L-R) to the approaching particle and the radius R of the metal particle. Thus, the closer the external charge to the metal surface and the smaller the size of the particle is, the larger the dipole moment and, thus, the stronger the attractive dipole-dipole interaction between two particles becomes. Another important fact is that attractive dipole-dipole interactions are significantly weaker and more dependent on the distance ($\sim 1/r^3$) than the repulsive interaction between monopoles ($\sim 1/r^2$).

It is useful to consider this attractive electrostatic energy quantitatively, assuming one ion with a charge e^- at a distance of 0.2 nm (close to the ionic radius of Br$^-$) from a non-grounded neutral metal sphere with a radius of 3 nm. The electrostatic energy of interaction is then -147 kJ/mol. Note that an approaching electrically neutral molecule would not lead to this type of electrostatic interaction. However, weak interaction due to dipole or higher multipole moments is possible.

The electrostatic interaction energy depends on the number of ions around the nanoparticle (for simplicity we assume equal distance from the sphere and equal charge). This energy increases with growing number of ions (N) and becomes positive for $N \geq 9$ (see Table 2). The electrostatic attraction energy is very high, when only few charges approach the nanoparticles and in magnitude is comparable with the energy of chemisorption. With increasing number of approaching charges, the energy becomes significantly smaller, which is particularly important in steric conception of nanoparticle stabilization as described below.

When nanoparticles are approached by more than one molecule (or ion), the system becomes more complex. For example, from basic vector algebra, the overall dipole moment is reduced to zero in case of two adsorbates of the same charge approaching opposite sides of the nanoparticle and enhanced, if they are of opposite charge. Collectively, cations and anions approaching the metal particles (assuming here equal probability to approach) induce many image charges δ^+ and δ^- on the surface (Fig. 2) and the particle obtains a multipole moment. As cations and anions often have a different chemical nature resulting in distinctly different interactions with the metal sphere, the metal surface is frequently surrounded predominately with one sort of ions and a shell of counter ions.

Thus, a single ion interacts very strongly with a non-charged non-grounded metal particle, as long as the number of equal ions around the nanoparticle is small. When the interaction of the metal particle with cations and anions is different, a double layer of oppositely charged ions can be formed. This double layer leads to repulsive forces between two nanoparticles in vicinity,[27, 28] whereas induced electric dipole moments (or higher order multipole moments) promote the approach of metal nanoparticles. It is interesting to note that changes in the magnitude of the dipole moments located close to the surface of the metal nanoparticle can be utilized for controlled agglomeration (when the dipole moment is high) and re-dispersion (when the dipole moment low) of the corresponding nanoparticles. This concept has been

applied in the design of "smart" nanomaterials.[41-43] It is important to note that we assumed the nanoparticles to be ideal metal spheres without considering the influence of quantum effects on the electronic structure of the nanoparticles. These effects may be particularly relevant to particles smaller than 1 nm. For a more detailed description of quantum properties of metal nanoparticles in a dielectric environment, we refer the reader to the Effective Medium Theory [44-46] and Green's Function based approach.[47]
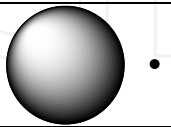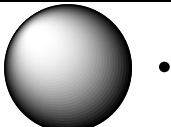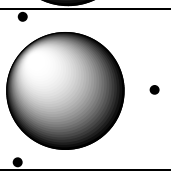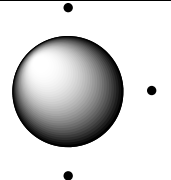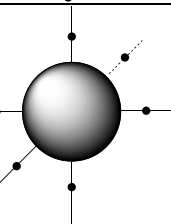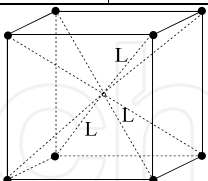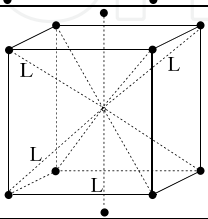
Number of charges	Geometry	Electrostatic interaction energy, kJ/mol
1		-147
2		-126
3		-106
4		-86
6		-50
8		-16
10		+24

Table 2. Idealised geometry of ion(s) with charge *e* approaching a neutral non-grounded metal sphere and corresponding electrostatic interaction energies between one of the ions and the metal sphere. *L* is the distance between the approaching ions and the centre of the sphere. For *N ≥ 8*, only the distances (L) to the external charges are shown, while the metal sphere is omitted. For the assumptions refer to the text.
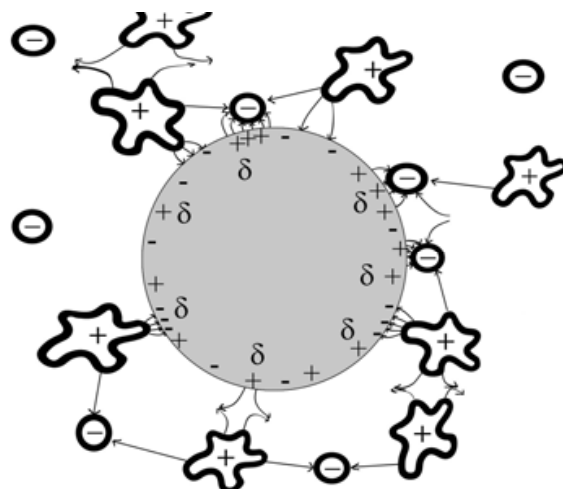
Fig. 2. Schematic representation of a metal particle surrounded by interacting cations and anions, leading to an alternating surface charge distribution.

2.2 Steric stabilization

Another stabilization mechanism is based on the steric repulsion between molecules or ions adsorbed on neighbouring particles. Size and chemical nature of these molecules determine the degree of stabilization. Due to geometric constraints around nanoparticles, large, bulky molecules provide a particularly effective stabilization and an elongated or conical geometry is advantageous to keep the approaching nanoparticles apart (Table 3 A).

Table 3. Schematic illustration of steric stabilization: *A* – Elongated or conical molecules adsorbed *via* anchoring centres (small black dot) hinder nanoparticles from close contact. *B* – Long polymer threads encapsulate a nanoparticle. *C* – Chelate effect, when the stabilizer is adsorbed *via* more than one anchoring centre (small black dots).

When the length of the stabilizer is significantly longer than the characteristic size of the nanoparticles, a sphere can be formed encapsulating the nanoparticle (Table 3 B). Because of that, high molecular weight polymers are often employed as stabilizers for nanoparticles.

Another important requirement is that the stabilizer has to be adsorbed strongly enough on the surface of the nanoparticles to provide long residence time and to prevent its spontaneous desorption. When a stabilizer provides more than one adsorption centre, the chelating effect can increase the probability that the stabilizer remains adsorbed (Table 3 C). Frequently, chemisorption is the driving force for strong binding between adsorbate and metal surface. Metals with more valence orbitals than valence electrons have an "electron-deficient" surface. Thus, molecules readily "donating" electron density (*i.e.* with chemical groups associated with free electron lone pair, such as divalent sulphur, trivalent phosphorus and trivalent nitrogen moieties or molecules with π-electrons, *e.g.*, aromatic systems) often adsorb very strongly on metal surfaces (although the opposite examples are also known [48, 49]). Strongly adsorbing, large molecules are prime candidates for stabilization of nanoparticles.

The concept of steric stabilization plays a very important role in the successful synthesis of nanoparticles. It is not restricted to metals, and can be applied on its own.

2.3 Stabilization by ionic liquid

The idea to employ bulky and highly charged adsorbents in the stabilization of nanoparticles rather than a neutral stabilizer results in the so-called electrosteric stabilization. The best stabilizers for nanoparticles are those, which are ionic, adsorb strongly enough and meet the conceptions of steric and electrostatic stabilization simultaneously.

Ionic liquids, consisting of cations and anions only, provide a huge excess of ions favouring coordination also of less strongly coordinating ions. Note that strong coordination is good for physical applications of the nanoparticles, *e.g.*, as quantum dots, but is not suitable for applications, such as catalysis, where access of the substrate molecules to the metal surface is required. It is worth to mention that nanoparticles with strongly adsorbing ligands can be isolated from excess stabilizer and isolated as powder, whereby the layer(s) of stabilizer on the surface is maintained.[50, 51] This test can be used as criterion for a particularly good stabilization of the nanoparticles.[30]

Due to the high ion density, ionic liquids enable particularly strong electrostatic stabilization, while at the same time they can be selected in such a way that either the cations or the anions are strongly chemisorbed, and either the cations or the anions have the appropriate bulky geometry. The bromide anions of tetraoctylammonium bromide ($[N_{8,8,8,8}^+][Br^-]$), for example, adsorb very strongly on many metal surfaces, while they have a relatively small size. The tetraoctylammonium cation on the other hand provides the bulky geometry necessary for steric repulsion. In fact, many examples for $[N_{8,8,8,8}^+][Br^-]$ stabilized metal nanoparticles are reported in the literature.[50] Charged polymers functioning as polyelectrolytes [52] are other well known stabilizers of metal nanoparticles [53-57] as well as metal oxide nanoparticles [58] and organic micelles.[59-61] They meet the conceptions of steric and electrostatic stabilization simultaneously, *i.e.*, they provide electrostatic stabilization.

Metal nanoparticles stabilized by tetraalkylammonium halides were reported for the first time in 1979.[62] Later, these nanoparticles were prepared *via* chemical reduction in the liquid phase [63] or electrochemically.[64] Thus obtained nanoparticles are stabilized by electrochemical and steric conceptions, as halogen ions adsorb very strongly on the metal

surface, while the surrounding tetraalkylammonium cations constrain close contact between the nanoparticles as illustrated in Fig. 3. Although tetrahexyl-, tetrabutyl- and tetraoctyl-ammonium bromide (and chloride) have a melting point around 100°C and above (and are therefore classified as molten salts), they provide the first examples describing the ability of ionic liquids to stabilize nanoparticles.[63, 64] Note that the use of imidazolium based ionic liquids for the stabilization of Ir nanoparticles was reported much later in 2002.[65]
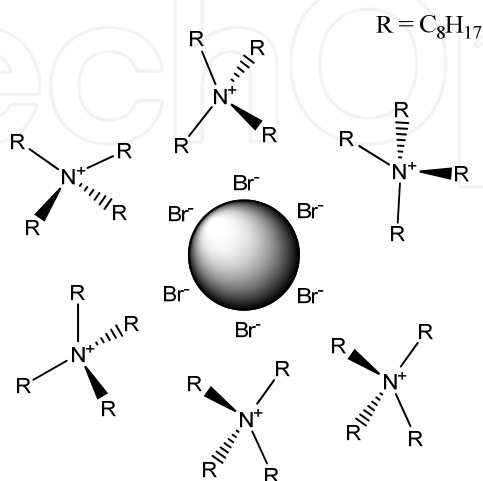

Fig. 3. Schematic illustration of the electric double layer around a tetrahexylammonium bromide stabilized metal nanoparticle as an example of electrosteric (combined electrostatic and steric) stabilization.

Another aspect of ionic liquids is that the thermal movement of the colloidal nanoparticles is suppressed due to the high viscosity of the surrounding medium minimizing the probability of close contacts. Let us analyse this aspect in further detail. Let us assume that nanoparticles with size $a = 3$ nm have just formed and are dispersed at room temperature (20°C) in a medium with viscosity η at a volume fraction φ of 0.01. To assess qualitatively their half-life time, we assume here a very simple model of rapid random coagulation, where every collision of two nanoparticles immediately leads to coagulation and, in consequence, agglomeration. The number of collisions v that one nanoparticle experiences per time unit with other nanoparticles can be expressed by eq. 4,[66] which can be obtained based on the Einstein–Smoluchowski [67, 68] formalism of Brownian motion of colloidal particles.

$$v = \frac{kT}{\pi \eta a^3} \varphi \qquad (4)$$

The inverted number of collisions per unit of time (eq. 5) is the time constant τ for rapid coagulation. This half-life time is a measure for the decrease of the concentration $c(t)$ of nanoparticles (eq. 6) with time.[66]

$$\tau \sim \frac{1}{v} \qquad (5)$$

$$\frac{c(t)}{c(t=0)} = \frac{1}{1 + t/\tau} \qquad (6)$$

Typical collision frequencies ν and time constants τ for such rapid coagulation for 3 nm sized particles in dependence of the viscosity of the surrounding medium are collected in Table 4. Since the viscosity of a typical ionic liquid is a factor of hundred or thousand higher than that of commonly used organic solvents, such as tetrahydrofuran (THF), the collision frequency becomes hundred and thousand times smaller. This results in a longer half-life time of the nanoparticles. Thus, ionic liquids are characterised by very low self diffusion coefficients [69-71] of approximately 10^{-12}-10^{-11} m^2/s compared to 10^{-9} m^2/s for classic solvents with viscosities similar to water (1 mPa s).[72] Although suppressed diffusion in media with high viscosity, cannot be the only mechanism for stabilization of small particles (the absolute values of half-life are still very small ~10^{-4}-10^{-3} s), the effect may contribute considerably to the overall stabilization of nanoparticles in ionic liquids, as is discussed below.

Medium	Viscosity, mPa s	Diffusion constant of nanoparticles, m^2/s	Collision frequency, 1/s	Half-life time, s
THF	0.46	$2 \cdot 10^{-10}$	10^6	10^{-6}
[C$_4$MIm$^+$][Tf$_2$N$^-$]	60 [73]	10^{-12}	10^4	10^{-4}
[C$_4$MIm$^+$][PF$_6^-$]	376 [73]	$2 \cdot 10^{-13}$	10^3	10^{-3}
Solid body	~10^{15}	10^{-25}	$5 \cdot 10^{-10}$	10^9

Table 4. Diffusion constant and estimated half-life time of 3 nm sized particles in environments with different viscosity assuming rapid coagulation at room temperature (see text).

The half-life time of the particles will be longer, if we assume the presence of surface species, which act as stabilizer (a coagulation probability of $1/10^6$ may be reasonable for collisions between two nanoparticles). In this case, a typical half-life time of colloidal particles calculates to half an hour in a highly viscous medium, whereas in classic solvents it would be in the range of seconds. The situation changes drastically, when the temperature of the surrounding medium is below its melting point. In this case, the ionic liquid is in a solid or quasi-solid,[74] *i.e.*, amorphous glassy state [75] with very high viscosities in the range of ~ 10^{15} mPa s. Embedded nanoparticles experience practically no Brownian movement and the half-life time is in the order of magnitude of 10^3 years. This effect may be applied to storage of nanoparticles for very long times in solid matrices of ionic liquids, until they are being used. Another potential application lies in the field of electrochemistry or photochemistry, when semiconductor nanoparticles serve as quantum dots or photoactive elements for solar cells.

In summary, suppressed diffusion of nanoparticles in highly viscous media, such as ionic liquids, leads to an increase in the lifetime by a factor of 10-1000 compared to classic low viscous solvents, contributing significantly to the stabilization of colloidal nano-sized particles. As mentioned above, ionic liquids can also serve as electrostatic and steric stabilizers. The physicochemical properties of ionic liquids and, thus, the properties of ionic liquid stabilized nanoparticles can be readily adjusted by changing cations and anions. Compared to polymers, ionic liquids as stabilizers for nanoparticles provide some particular advantages. Non-ionic polymers (in contrast to polyelectrolytes) have no ionic nature (only steric stabilization applies) and their ability to dissolve various compounds, for instance, metal precursors or substrates is limited (*vide infra*). Thus, often an organic solvent is required, where both polymer, metal precursor and the substrate are soluble (*e.g.*, in case of applications in catalysis). The use of organic solvents can be avoided, when catalytic reactions are performed in neat ionic liquids (with dispersed nanoparticles). Reactions can also be conducted in neat substrate, where small amount of ionic liquid stabilized nanoparticles are added.

As we have mentioned above, strongly adsorbed species are needed for good stabilization of nanoparticles. Many ions generally employed in ionic liquids, like the cations tetraalkylammonium ($N_{k,l,m,n}^+$), tetraalkylphosphonium ($P_{k,l,m,n}^+$), and 1,1-dialkyl-pyrrolidinium ($C_mC_nPyr^+$) and the anions bis(trifluoromethanesulfonyl)amide (Tf_2N^-), trifluoromethanesulfonate ($CF_3SO_3^-$), alkylsulfate ($C_nOSO_3^-$), tetrafluoroborate (BF_4^-), hexa-fluorophosphate (PF_6^-) are weakly coordinating and, thus, need to be complemented with an appropriate counter ion to stabilize nanoparticles efficiently.

On the other hand, there are reports on the ability of BF_4^- to coordinate to metallic Ir and act as a stabilizer for Ir nanoparticles.[76, 77] Addition of 1,8-*bis*(dimethylamino)naphthalene (PS) provided improved stability, yet transmission electron microscopy (TEM) showed assemblies typical for the early stages of agglomeration. The PS may serve as a proton scavenger or the two tertiary amino groups of PS act as an anchor for strong adsorption. Also the bulky geometry of PS may be beneficial for steric stabilization. After addition of excess [N_{4444}^+][BF_4^-] (melting point 155°C), the life time of the nanoparticles increased significantly,[77] most likely, due to the increased viscosity of the surrounding medium and, thus, reduced Brownian diffusion.

On the contrary, Ir nanoparticles prepared in [C_4MIm^+][PF_6^-], [C_4MIm^+][BF_4^-] and [C_4MIm^+][$CF_3SO_3^-$],[76] were found to be very stable possibly due to the formation of strongly coordinating *N*-heterocyclic carbenes (*vide infra*).[78]

Various physical properties of ionic liquids, as viscosity and molar concentration, are directly dependent on the sum of the ionic volumes of cation and anion.[72] In this light, it is interesting to consider the effect of the choice of the ionic liquid. The size of the nanoparticles frequently increases with increasing molecular volume (or size) of the (weakly) coordinating anion (BF_4^-, PF_6^- and Tf_2N^-), *e.g.*, for Ag nanoparticles from 2.5 to 27 nm [79] and for W nanoparticles from 1.5 to 30 nm.[80]

The size of the ion determines the distance from the surface of the nanoparticle and the number of ions around it. This influences directly the total electrostatic energy of the system. In the case of weakly coordinating ions, the interaction energy with the metal particle is almost only electrostatic in nature and its value depends on the particle size and the distance between particle and the ion and can reach up to 100 kJ/mol. The size of the ion determines also the maximum number of ions, which can be accommodated around a nanoparticle. In result, the thickness of the electric double layer is influenced and, thus, the stability of nanoparticles in terms of the electrostatic conception.

Halogens (Cl^-, Br^-), dicyanimide (($CN)_2N^-$), carboxylates ($RCOO^-$), *etc.* adsorb strongly on metal surfaces and, thus, provide good stabilization. It is important to note that even traces of halogens, as present in many commercially available ionic liquids in concentrations of several tens to hundred ppm, may contribute to the stabilization of the metal nanoparticles.[30] The contribution of the cation to the stabilization of the nanoparticles also has to be taken into the account.[80] Bulky imidazolium cations, such as 1-alkyl-3-methylimidazolium (C_nMIm^+) as well as ions, such as 1-alkylpyridinium (C_nPy^+) may contribute to varying degree to the stabilization of the nanoparticles. Functionalized ionic liquids [81] (often, but not necessarily, imidazolium based) with a specific coordinating group attached to the structure of cation or/and anion can be used for enhanced stabilisation. Alkylnitrile pyridinium [$N{\equiv}CC_nPy^+$] and 1-alkylnitrile-3-methylimidazolium [$N{\equiv}CC_3MIm^+$] based ionic liquids, *e.g.*, provide better stabilization of Pd nanoparticles [82, 83] than alkyl pyridinium ionic liquids [C_nPy^+] and 1-alkyl-3-methylimidazolium [C_nMIm^+] based ionic liquids. Pt and Ru nanoparticles were also stabilized successfully in 4,5-dicyano triazolium based ionic liquid.[81] Thiol functionalized

imidazolium ionic liquid, specifically 1-mercaptoalkyl-3-methylimidazolium, was found to be an excellent stabilizer for, *e.g.*, Au nanoparticles.[84] The strong adsorption of carboxylic groups on metal surfaces [85, 86] makes ions carrying one or a few carboxylic groups to be very attractive for the stabilization of metal nanoparticles. Pivalic (Piv-), tartaric (TA^{2-}), Glycinate (Gly^{2-}) as well as malic acid (MA^{2-}) based ionic liquids, combined with long-chain tetraalkylammonium cations are good to excellent stabilizers for, *e.g.*, Pt, Pd, Rh, Ru and Ni nanoparticles.[87, 88]

It is interesting to note that even non-functionalized imidazolium-based ionic liquids with weakly coordinating anions are stabilizers for various transition metal nanoparticles.[76, 89-92] Explanations may be that (*i*) the imidazolium cation can, in principle, adsorb on the metal surface *via* its π-electron system and (*ii*) imidazolium cations, which are not substituted in 2-position, can form *N*-heterocyclic carbenes, which are strongly coordinating to many metals.[93-96] On the other hand, the strong adsorption of carbenes results in poisoning of the metal surface. This type of inhibition was demonstrated for the hydrogenation of acetone over Ir nanoparticles in imidazolium-based ionic liquids.[78]

Additives can be used to further stabilize nanoparticles in imidazolium based ionic liquids. Stabilization with polyvinylpyrrolidone (PVP) is necessary to obtain stable mono- and bimetallic Pt/Au nanoparticles immobilized in [C$_4$MIm$^+$][PF$_6^-$].[97] Also, ionic liquid-like copolymers can be used to stabilize Rh [98] and Pt [99] nanoparticles, where [C$_4$MIm$^+$][BF$_4^-$] itself can not stabilize the platinum nanoparticles sufficiently.[99]

2.4 Stability against oxidation

When metals are exposed to air, dioxygen is adsorbed on their surface, often accompanied by dissociation of the dioxygen. This is the first step to oxidation of metals with low standard electrode potential (*e.g.*, Ni, Fe, Cu, Co). Monooxygen on the surface of metals with high standard electrode potential (*e.g.*, Au) does not lead to noticeable oxidation of the metal at normal conditions. The oxidation of metals is a highly complex process,[100] whereby dissociative adsorption of oxygen on the metal surface constitutes a key step. A straightforward idea of protecting the metal from oxidation is to prevent the adsorption of oxygen. In other words, one can modify metal surfaces with protective agents before exposing them to air. In the best case, agents stabilizing against agglomeration act at the same time as a protective agent against oxidation.[101] Generally, the adsorption energy of the stabilizer has to be significantly higher than the adsorption energy of monooxygen on the same adsorption site. However, it is difficult to choose a proper stabilizer *a priori*. It is easier to prepare nanoparticles with a chosen stabilizer and then check, if it protects the surface of the nanoparticles from oxidation. Ni nanoparticles protected (and stabilized) with [N$_{8,8,8,8}^+$][Br$^-$] prepared *via* the wet chemical way (*vide infra*) [63] are stable in air and keep the dark-brown colour specific for metal colloids for more than 2 years. In contrast, [N$_{8,8,8,8}^+$][Br$^-$] stabilized Ni nanoparticles prepared *via* electrochemical reduction [64, 102] were found to be extremely oxygen sensitive. The stability of metal nanoparticles against oxidation can also be size dependent. Under oxygen plasma conditions, 1.4 nm sized Au nanoparticles showed better oxidation resistance compared to larger particles.[103] A similar effect was predicted for Pt nanoparticles.[104]

3. Design of metal nanoparticles in ionic liquids for specific applications

The task for which nanoparticles are to be used often determines the preparation strategy. In the case, when access to the surface of the nanoparticles is not needed, one can choose a

stabilizer, which adsorbs very strongly on the surface of nanoparticles (*vide supra*). Au nanoparticles, *e.g.*, are often used as quantum dots in applications, where their optical properties are important (*e.g.*, in cancer cell imaging).[105] In these cases, stabilizers such as tetraalkylammonium bromide [105, 106] or bulky, divalent sulphur containing molecules [107-109] are commonly employed.

For applications of nanoparticles in catalysis, a balance between the adsorption strength of the stabilizer and the substrate has to be found. Stabilisation with strongly coordinating adsorbents results in a reduced or completely suppressed activity. Besides the well-know surface poisoning effect induced by divalent sulphur,[110, 111] the presence of halogens can poison the metal surface.[86] In fact, $[N_{8,8,8}^+][Br^-]$ stabilized Ni nanoparticles were found to be completely inactive in the hydrogenation of, *e.g.*, aliphatic ketones and *β*-ketoesters, while PVP stabilized Ni nanoparticles demonstrate high catalytic activity in these reactions.[198] As stabilizer and substrate molecules compete for coordination to the metal surface, the poisoning effect may vary in dependence of the substrate molecule. Rh nanoparticles, *e.g.*, catalyze the hydrogenation of benzene, while they show no activity in the hydrogenation of aliphatic ketones. Similarly, Ru nanoparticles stabilised by $[N_{8888}^+]_2[TA^{2-}]$ or $[N_{8888}^+]_2[Gly^{2-}]$, catalyze the hydrogenation of nitrobenzene to cyclohexylamine, while $[N_{8888}^+]_2[Me_2Gly^{2-}]$ stabilised Ru nanoparticles provide aniline.[88] Selective surface poisoning can be utilized to direct selectivity, as is illustrated by the example of enantioselective hydrogenation of *β*-ketoesters, when a small amount of Br⁻ ions added to tartaric acid modified Ni particles resulted in higher enantioselectivity.[86] Functional groups can be introduced into the ionic liquid to combine the stabilization effect with additional properties, such as a co-catalytic group, a proton buffer or chirality.

4. Preparation concepts for ionic liquid stabilised metal nanoparticles

Methods for the synthesis of nanoparticles have a more than 150 year old history dating back to the work of Faraday in 1857.[112] It appears logical to employ these methods also in the synthesis of ionic liquid stabilized nanoparticles. Herein, we give an overview on strategies to obtain nanoparticles in general and ionic liquid stabilised particles in particular. For an overview on metal nanoparticles and stabilizers we refer the reader to the corresponding review articles [8, 14, 30, 101, 113-127] and for more detailed procedures to the original literature.

In general, the preparation methods for nanoparticles are classified as "top-down" and "bottom-up" approaches.[101, 128] Herein, we do not consider classic "top-down" methods, which deal with mechanic grinding of bulk metals to the nano-sized scale. We will rather focus on "bottom-up" (starting from molecular metal precursors) and a combination of "top-down" and "bottom-up" strategies. The basic idea is to obtain metal atoms (from bulk material) and to control the nucleation and growth to nano-sized scale. For clarity, we call "bottom-up" methods *chemical*, due to chemical reduction of metal precursors to neutral atoms. Methods being combinations of "top-down" and "bottom-up" we call *physical*, as the formation of metal atoms (from bulk metals) often involves various physical techniques.

4.1 Chemical methods

Typically, a precursor to the metal of interest (such as an inorganic salt or an organometallic complex) is reduced (or decomposed) to generate neutral metal atoms. In the absence of stabilizers, the atoms quickly agglomerate to microscopic crystallites. Coagulation of these

crystallites leads to precipitation of the metal as "metal black". It is very difficult to directly measure the size of nanoparticles, while they are growing.[129] An indirect method for following the kinetics of nanoparticle formation deals with the hydrogenation of cyclohexene as probe reaction.[30] A recent *in situ* electron microscopy study describes the dynamics of the growth of Pt nanoparticles under typical synthesis conditions.[130] Along with the conventional growth mechanism by incorporation of metal atoms from solution, frequent coalescence events between the particles were observed.[130]

In the presence of an appropriate stabilizer, it is possible to halt the nucleation at a certain stage and to obtain colloidal nanoparticles. Besides the appropriate choice of the stabilizer, careful selection of the metal precursor, the reducing agent, and the solvent are also important. Stabilizer and reducing agent have to be soluble in the solvent employed, while it is not necessary that the metal precursor is soluble.[131]

The associated processes during formation of nanoparticles are summarized in Fig. 4. Typically, metal atoms are formed by reduction (1) or decomposition of the metal precursor (2A). Free atoms are highly unstable and nucleate (3) quickly, until this process is prevented by a stabilizer (4). The reducing agent may also act as a stabilizer.[101] The range of suitable metal precursors can be expanded by employing strongly reducing agents (or harsh reaction conditions), while decomposition of the reducing agent or reaction with the stabiliser has to be avoided. By-products formed from the metal precursor (2B) can adsorb on bare or stabilized nanoparticles, which can lead to reduced stability or/and surface poisoning.[110] Some by-products (*e.g.* strong acids and bases) can also lead to decomposition of the stabilizer. In order to avoid these problems metal precursors, reducing agent, and stabilizer have to be carefully chosen, especially when ionic liquids are employed as stabilizers.
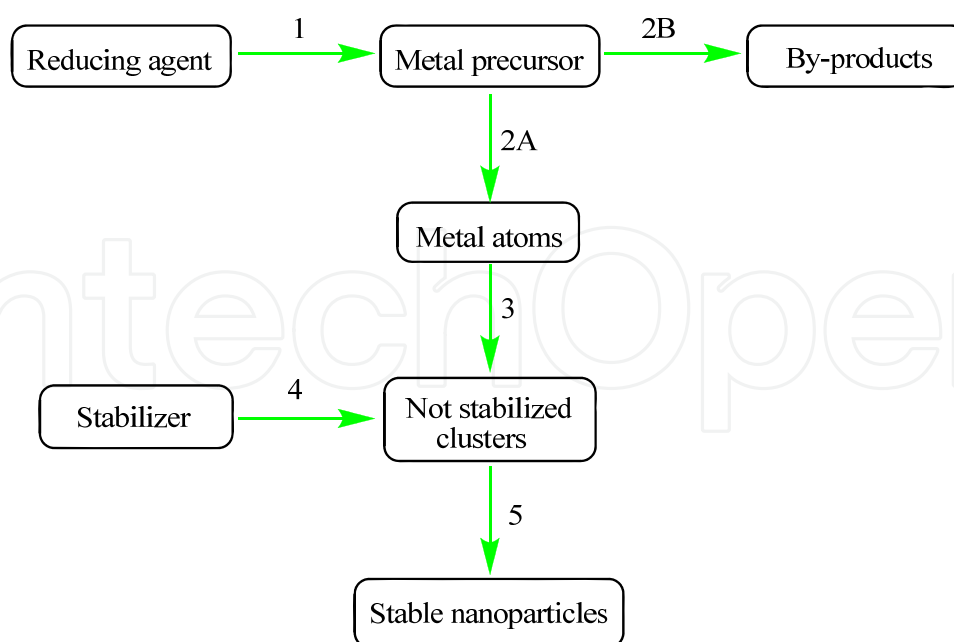

Fig. 4. Schematic sequence of the formation of metal nanoparticles.

The chemical stability of ionic liquids has to be taken into the account, when they are used as stabilizers for nanoparticles. Ionic liquids often react with strong bases, acids, some reducing agents (*e.g.* $NaBH_4$, $LiAlH_4$, $Al(alkyl)_3$, *etc.*) or may decompose at relatively high temperatures. Preferentially, mild reducing agents, like hydrogen or alcohols should be used. This requirement limits the selection of appropriate metal precursors. Preferably, hydrogen or reducing agents, which give non-coordinating, volatile, non-reactive by-products, are used at temperatures below the decomposition temperature of ionic liquids. An elegant way to avoid the decomposition of ionic liquids by acids HX (X = NO_3^-, BF_4^-, PF_6^- or $CF_3SO_3^-$) produced during reduction of AgX is the addition of an imidazole scavenger, which resulted in increased stability, narrowed size distribution and decreased average size of the Ag nanoparticles formed.[79]

Interestingly, if the metal precursor is soluble in ionic liquids (sometimes this generally slow process can be speeded up by stirring, heating, ultrasonic treatment or addition of a few drops of a suitable solvent), the use of additional organic solvents is no longer needed. For instance, the Ru precursor $[Ru(MeAllyl)_2(COT)]$ (COT = cyclooctatetraen) is soluble in $[N_{8,8,8}^+][Piv^-]$ and can be reduced easily with hydrogen, while this ionic liquid successfully stabilizes the Ru nanoparticles and protects the Ru surface from oxidation for a long time. Other examples describing the preparation of nanoparticles in ionic liquids *via* the chemical route can be found elsewhere.[8, 30, 89, 91, 121, 122, 132-134] The preparation steps of this so-called direct route are schematically illustrated in Fig. 5.
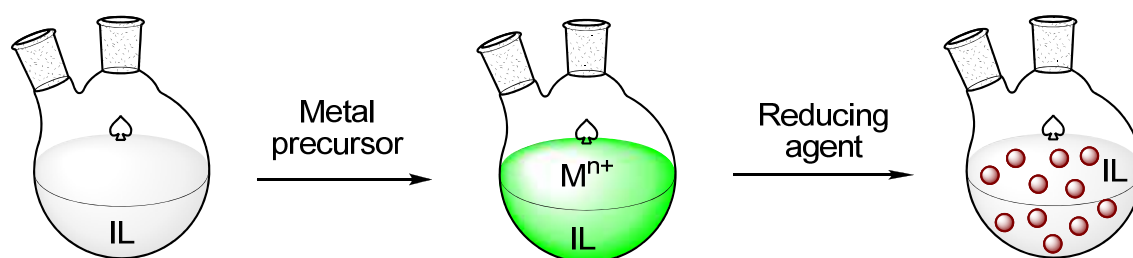

Fig. 5. Preparation of nanoparticles in ionic liquids *via* direct method. In the first step a suitable metal precursor is dissolved in the ionic liquid (IL), followed by reduction with a suitable reducing agent or heating the mixture to decompose the metal precursor.

A major advantage of the direct method is its simplicity. However, it cannot always be applied, as only few metal precursors meet the above-mentioned requirements. In case of difficulties in preparing nanoparticles directly in ionic liquids, the following alternative approach (indirect method) may be considered. The nanoparticles of interest are prepared using a convenient and suitable combination of stabilizer, metal precursor and reducing agent in an organic solvent and then transferred into the required ionic liquid (preferably after isolation of the nanoparticles or removal of the by-products, excess reducing agent, stabilizer and solvent); the indirect method is illustrated in Fig. 6. Note that the stabilizer has to be well soluble in the solvent in order to obtain a good dispersion of thus prepared nanoparticles.

Tartaric acid based ionic liquids $[N_{6,6,6,6}^+][TA^-]$, *e.g.*, are not stable against strong reducing agents as, *e.g.*, $NaBH_4$. Therefore, the reduction of metal precursors in the presence of such ionic liquids needs to be avoided. Nonetheless, $NiCl_2$, *e.g.*, can be reduced with $NaBH_4$ in a classic solvent in the presence of PVP (polyvinylpyrrolidone) as stabilizer. Then, thus prepared nanoparticles can be isolated and transferred into the ionic liquid of interest.see, e.g.,[135]
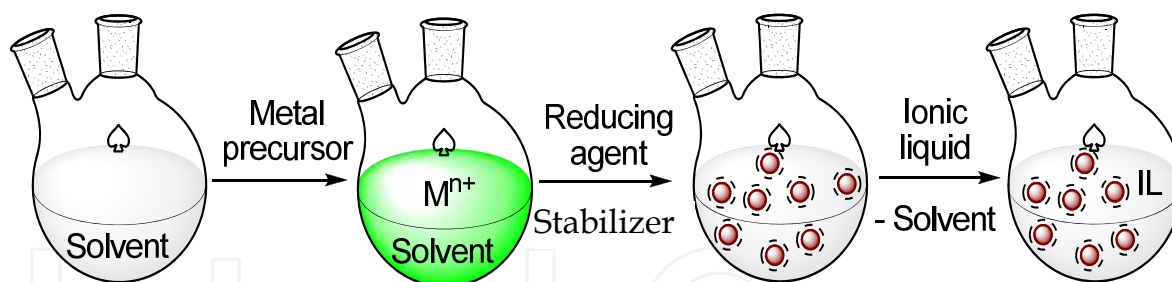
Fig. 6. Indirect method for the synthesis of nanoparticles in ionic liquids. After dissolution (not always needed) of the metal precursor in an organic solvent, the former is reduced in the presence of an external stabilizer, then the ionic liquid (IL) is added and solvent (and any by-products) are removed.

Another example is the precursor [Ni(acetylacetonate)$_2$], which can be reduced readily with Al(^{i}Bu)$_2$H in THF solution. Then, after addition of ionic liquid and removal of solvent very stable and air insensitive Ni nanoparticles of ~ 2-3 nm size (Fig. 7) are obtained and can be used, *e.g.*, in the hydrogenation of ketones and ketoesters.[87]

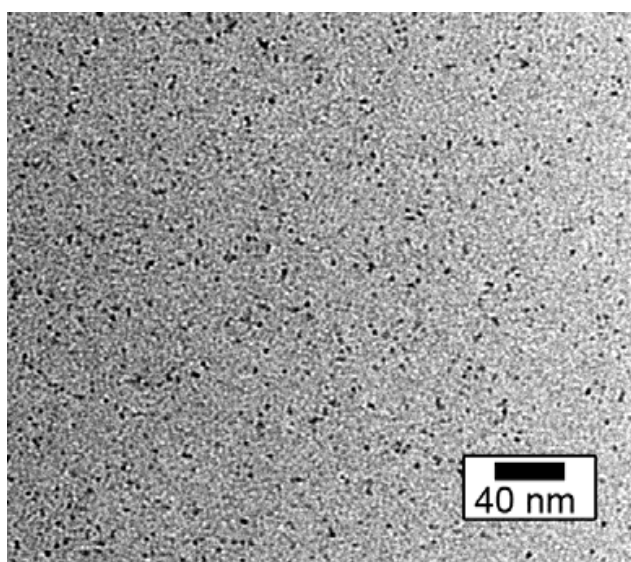Fig. 7. TEM image of Ni nanoparticles immobilized in [N$_{6,6,6,6}$$^+$][TA$^-$] prepared *via* the indirect method, see text for details.

4.2 Physical methods

As mentioned above, nanoparticles can be prepared *via* a combination of "top-down" and "bottom-up" routes. First, free metal atoms are obtained *via* a chosen physical method and their subsequent agglomeration is controlled by a stabilizer. Below we give a short overview of some of these physical methods, which found attention in the past or recent literature.

4.2.1 Solvated metal atoms

If one would think about methods to obtain free metal atoms, the first idea, which might come to mind, is to transfer solid bulk metal to the gas phase through strong heating in ultra high vacuum. In fact, condensation of the metal vapour together with a weakly stabilizing organic solvent (pentane, acetone, THF) at low temperature (-196 °C) (so called metal-

vapour synthesis) results in solvent pre-stabilized metal clusters, consisting of a few atoms (5-10).[136] These are stable at low temperatures (typically below -50 °C), while a precipitate of a finely dispersed metal powder forms rapidly at ambient temperatures. In order to avoid agglomeration, additional stabilizers have to be used. In fact, mono-dispersed 4-5 nm sized Au nanoparticles were obtained *via* metal vapour synthesis, quick reaction with dodecanethiol after warming up and "digestive ripening" by refluxing in toluene.[137] This method can be applied to other metals and stabilizers,[137-145] including ionic liquids. Note that this method can be scaled up easily. In a slightly different approach, Au and Ag can be sputter deposited onto $[C_4MIm^+][PF_6^-]$ to obtain monometallic and bimetallic Au and Ag particles with 3-5 nm diameter.[146, 147]

4.2.2 Laser ablation

Nanoparticles of various metals (including bimetallic particles [148-155] and metal oxides [156-160]) can be made by laser ablation methods. Instead of using chemical precursors, the laser ablation method deals with precursors in form of macroscopic metal plates or relatively "large" nanoparticles (100 nm in size and larger), which are submerged in a solvent. When focused on a very small spot of the metal surface, laser ray induces quick heating and subsequent transport of metal atoms to the liquid medium. If the later contains a proper stabilizer, the atoms nucleate to stable metal nanoparticles. Au nanoparticles can be prepared *via* laser ablation from Au foil in neat ionic liquids.[161] It is interesting to note that $[C_8MIm^+][BF_4^-]$ provided better stabilities compared to ionic liquids with shorter alkyl-chains, such as $[C_4MIm^+][BF_4^-]$ and $[C_2MIm^+][BF_4^-]$.

Laser irradiation can also fragment existing nanoparticles.[162] The efficiency of nanoparticle formation depends on the frequency of the laser pulses applied, the pulse duration time, pulse power and the wavelength of the laser. It is interesting to note that the nanoparticles are most efficiently heated, when the wavelength of laser irradiation matches the frequency of the plasmon absorption band.[163]

Laser ablation [164] is a relatively new, not fully investigated, and not widely used (in comparison with numerous chemical methods) method for the synthesis of nanoparticles. Reports on catalytic application of nanoparticles made by laser ablation are limited.[165] A particular disadvantage is the slow preparation, although the laser beam can be split into several beams. Typically, only 4-5 mg of Pt nanoparticles is produced after 1 hour of laser work. This can be accepted in the case of model catalysts, where the material demonstrates excellent catalytic properties or high metal loadings are not needed.

4.2.3 Electrochemical synthesis

In an electrochemical way of making metal nanoparticles, a solution of stabilizer (*e.g.*, tetraalkylammonium bromide in THF) is electrolyzed using an anode made of the metal of interest and an inert cathode.[64, 166] Under the conditions of the electrolysis, dissolution of the anode material takes place *via* oxidation. The metal cations transfer to the cathode, where reduction, nucleation and finally stabilization occur. The size of thus-prepared nanoparticles can be easily controlled by the current density. The method is applicable to many transition metals. Moreover, systems with two anodes of different metals result in the formation of bimetallic nanoparticles. When oxidation of the anode metal is difficult, the metal of interest can be introduced as inorganic salt.[167] Pd nanoparticles, *e.g.*, prepared *via* this method were found to be catalytically active in the Heck reaction [168] and the

hydrogenation of olefins [169] both as colloid (in propylene carbonate as solvent) and supported on alumina. Although the electrochemical reduction is very simple, it is not yet used for routine synthesis of metal nanoparticles. The approach can be adapted readily to the synthesis of nanoparticles in ionic liquids, whereby a metal precursor dissolved in ionic liquid is reduced *via* an electric current. Thus, Pd nanoparticles can be electrodeposited in pyrrolidinium based ionic liquids [170] and Au and Ag nanoparticles in imidazolium based ionic liquids.[171] The size, shape and morphology of the obtained nano-sized Au and Ag structures were found to be strongly dependent of the physical state of the reaction medium (solid or liquid).[171]

4.2.4 Plasma method

An interesting approach for preparation of nanoparticles in ionic liquids was recently found *via* plasma induced reduction of metal salts.[172-174] Ag,[175] Cu [176, 177] and Al [177] nanoparticles, *e.g.*, can be prepared by treating a solution of the corresponding salt in an ionic liquid with a low temperature ionized Ar plasma, which results in electron transfer into the liquid phase (close to the interface) and subsequent reduction of metal cations.

4.2.5 Electron beam or γ–irradiation

The method of reducing of metal cations employing an electron beam or γ-irradiation for making mono- or bimetallic nanoparticles (as well as semiconductor nanoparticles) is known since the late seventies.[178-182] and [183-186] Recently, this method found a practical application in nanolithography [187] for optical and electronic data transfer. High molecular weight polymers like polyvinyl alcohol (PVA) or poly(acrylamide) (PAM) were employed to stabilize the nanoparticles. Now it becomes logical to explore the use of ionic liquids acting as a stabilizer instead of a polymer. Thus, Au nanoparticles, *e.g.*, can be prepared in ionic liquid by electron beam irradiation.[188] In $[C_4MIm^+][Tf_2N^-]$, relatively large nanoparticles with average diameter ~120 nm were obtained.[188]

4.2.6 Photochemical method

Certain metal precursors can be reduced under UV irradiation. This process is often assisted by semiconductors,[189-192] which provide electrons generated after light induced excitation. Reduction of alkylpyridinium Au^{3+} complexes under UV irradiation provides Au particles, whereby size, shape, and morphology are strongly dependent on the physical state of the complex.[193] Thus, reduction in the solid state resulted in the formation of hexagonal platelets with a size of 10-20 μm. Small spherical particles in the range of 50-100 nm were obtained close and above the melting point.

4.2.7 Comparison of chemical and physical methods

A strong advantage of the physical methods for making nanoparticles is that no chemical reducing agent is involved, as laser ablation and metal vapour deposition methods do not require reduction, while metal cations are reduced by electric current in case of the electrochemical synthesis. The absence of chemical precursors and reducing agents significantly decreases the limitations in the synthesis of nanoparticles. Involving less chemical substances, nanoparticles with particularly high purity can be obtained that may be important in catalysis. In particular, the metal, which is employed in form of the bulk

metal, *e.g.*, as a thin foil, can be used in very high purity. However, physical methods generally require a specific apparatus (laser, solvated metal atom dispersion (SMAD) reactor, source of γ-rays, *etc.*). Such equipment is available on the market and can be adapted to the synthesis of nanoparticles.

A comprehensive comparison of the catalytic properties of nanoparticles obtained *via* chemical and physical routes is difficult, because of the scarce information on nanoparticles prepared *via* physical methods. Catalytic applications were described for Pd nanoparticles obtained *via* electrochemical route,[168, 169] and metal clusters obtained in a SMAD reactor.[138] The differences in the catalytic behaviour relative to analogous conventional catalysts obtained *via* chemical route [138] concerning activity and selectivity in, *e.g.*, the hydrogenation of 1-heptene or 1,4-butadiene lie not only in the size and shape of the particles, but also in specific interactions with the solvent. Thus, it is claimed that Pd nanoparticles, *e.g.*, react with polar solvent molecules and acquire a negative charge.[136] The absence of other chemical species, which can interact with the metal and the small size of the nanoparticles make them in some degree comparable with gas phase metal clusters and their unique reactivity.[194]

5. Conclusions

Ionic liquid modified nanoparticles are a system with many degrees of freedom and particularly interesting for applications in catalysis. As the physical properties (viscosity, conductivity, melting point, *etc.*) of ionic liquids can be tuned readily by changing the structure of cation and anion, the physical behaviour (solubility, dispersion, accessibility, *etc.*) of nano-sized catalysts can be tailored to specific applications. Functional groups can be introduced into the cation or anion in order to increase the stability of the nanoparticles and to tailor the catalytic properties, in particular, activity and selectivity. Note that simple mixtures of two (or more) ionic liquids with one or two sorts of nanoparticles will result in new physicochemical properties, which are different from those of the single components. Extending the preparation and use of monometallic nanoparticles immobilized in ionic liquid to bimetallic or semiconductor nanoparticles appears particularly interesting for further exploration and application. There are numerous reports about excellent catalytic properties of nanoparticles in ionic liquids. Particularly interesting are those cases, where the substrate is readily soluble in the ionic liquid utilizing the quasi-homogeneous nature of the suspended nanoparticles, and where the product separates readily from the ionic liquid phase. To extract the product, the reaction may be performed in biphasic systems (for example with supercritical carbon dioxide *sc*CO$_2$ as mobile phase) [195] or the ionic liquid with embedded nanoparticles is immobilized on a heterogeneous support.[135, 196] A conceptual review on molecular homogeneous and nano-sized catalysts immobilized in a thin film of ionic liquids supported on a heterogeneous carrier will be published in due course.[197]

6. Acknowledgment

7. References

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Edited by Prof. Scott Handy

This volume, of a two volume set on ionic liquids, focuses on the applications of ionic liquids in a growing range of areas. Throughout the 1990s, it seemed that most of the attention in the area of ionic liquids applications was directed toward their use as solvents for organic and transition-metal-catalyzed reactions. Certainly, this interest continues on to the present date, but the most innovative uses of ionic liquids span a much more diverse field than just synthesis. Some of the main topics of coverage include the application of RTILs in various electronic applications (batteries, capacitors, and light-emitting materials), polymers (synthesis and functionalization), nanomaterials (synthesis and stabilization), and separations. More unusual applications can be noted in the fields of biomass utilization, spectroscopy, optics, lubricants, fuels, and refrigerants. It is hoped that the diversity of this volume will serve as an inspiration for even further advances in the use of RTILs.

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