Effect of Ionic Liquid (emim BF$_4$) on the Dispersion of Gold Nanoparticles

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Abstract. A simple method has been described for the design of hybrid materials made of 1-ethyl-3-methylimidazolium tetrafluoroborate (emim BF$_4$) stabilized gold (0) nanoparticles providing clear evidence about the coordination and stabilization behavior of imidazolium ionic liquids. The monodispersed gold nanoparticles were thoroughly verified by steady state spectroscopy and TEM microscopy, the hybrid material in comparison with the bare Au nanoparticles. This study revealed enhanced emission and a red-shifted absorption band which is attributed to charge transfer from IL to gold nanoparticles. TEM images of the nanoparticles corroborated the steady state results and showed similar particle sizes furthermore the nanoparticles appear often surrounded by IL layers. Based on the experiment results, which favor the interaction between IL anions instead of IL cations, we suggest the existence of an Au---F interaction and anionic Au-BF$_4^-$ stabilization in the fluorine-containing ILs.

1. Introduction
In recent years, with advances in nanotechnology, various new nanomaterials have been investigated for application in the development of electrochemical sensors [1]. Composite of nanoparticles with ionic liquids represent a unique physical system where properties of the components wholly or partially mix and new behavior can emerge [2-4]. The combination of ionic liquids and nanoparticles are regarded as one of the very promising media whose function can be designed [4-10].

The study of the metal nanoparticles has been an incredibly active area in recent year because of their application in different domains, which will unlock new pathways in the field of nanotechnology [11]. As the name suggests, metallic nanoparticles are characterized by their small size and huge surface area to volume ratio, which allows for more points of contact than would be the case of their bulk equivalent compound, making them an excellent candidate for a variety of purpose in various fields [12, 16].

Among various metal nanoparticles, gold nanoparticles have tremendous interest in wide-ranging applications such as photonics, information storage, catalysis, electronic, therapeutics, and photovoltaics, [17, 18]. Bare metal nanoparticles are prepared by employing physical methods such as mechanic subdivision of metallic aggregates and evaporation of metal in vacuum by resistive heating or laser ablation and by chemical methods such as reduction of metal ions in a solution using appropriate reduction agents.

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However, it is well known that metallic NPs are only kinetically stable, and they have high tendency to aggregate and make bigger structure due to large surface energy that drives thermodynamically favored coalescence [23]. Consequently, to obtain a stable dispersion of Au-NPs freely dispersed in solution, it is necessary to find means to prevent this phenomenon either by functionalization during synthesis or by collecting the particles in a compatible medium before they agglomerate or aggregate [24-26]. In this context, Ionic liquids have emerged as one of the most investigated classes of stabilizing agent for nanoparticles, because they allow stable dispersion without the need for additional stabilizers [27, 28]. They are structured solvents that can act as a template for the shape-selective synthesis of nanoparticles. Moreover, the unique combination of non-volatility and favorable solubilizing characteristics of ILs has motivated a growing interest as a replacement for organic solvents and as a new way to study nonaqueous solubility of metallic nanoparticles [27].

Ionic liquids are the generic term for a class of materials constituted entirely of ions and being liquid below 100 C. These unique substances composed entirely of ions offer a host of attractive properties, including ultra-low vapor pressure, high thermal stability, high ionic conductivity and a broad redox stability [29, 30]. Ionic liquids are characterized by weak interactions between a large cation and charge delocalized anion. This feature produces unusual liquid-like transport properties [31]. Moreover, owing to their extremely low vapor pressures, ionic liquids can be treated under high vacuum conditions and are regarded as fruitful media for vacuum sciences and technologies [32, 33].

Herein we represent and discuss the contribution of ionic liquid (emim BF₄) in the dispersion and stabilization of metallic nanoparticles (Au-NPs) for future application in catalysis and chemical sensors as well as in plasmonics.

2. Experimental:
All reactions involving gold nanoparticles and ionic liquids were carried out under an argon atmosphere.

1.1. Chemicals
All chemicals were used as received from the manufacturer without further purification. Gold nanoparticles (50 nm) were purchased from NanoCS. 1-ethyl-3-methylimidazolium tetra fluoroborate [emim] [BF₄] (99% purity) were purchased from Sigma-Aldrich.

1.2. Characterization
Samples for UV-Vis measurements were carried out using a Genysys 10S UV-Vis-Spectrometer (Thermo Scientific). Fluorescence spectra were determined using a Horiba Fluoromax-4 spectro fluorometer. For solution measurements, a conventional 10mm quartz cuvette was used. Room temperature time-resolved photoluminescence measurements were conducted using time-correlated single photon counting (TCSPC) [18] with a GaAs photocathode as a detector. Excitation was achieved by a Hamamatsu laser diode at λ= 373 nm.

2. Results and discussion:
Additionally to their small size and their high surface area, metallic nanoparticles have strong tendency to aggregate [24-26]. Since they are unstable from the standpoint of agglomeration, and in the absence of any extrinsic impediment, the unprotected particles aggregate primarily under the action of Van der Waals forces. To prevent aggregation process from occurring, the particles surface can be protected by electrostatic stabilization and steric stabilization [34]. Electrostatic stabilization is based on the Coulomb repulsion between individual particles promoted by adsorption of ions on metallic surface leading to the formation of multilayers [35-37]. Steric stabilization is builds on the steric hindrance achieved by involving the metal center, and a sterically bulky layer material, such polymer or surfactant, forming a protective layer promotes a steric barrier preventing the coagulation or aggregation [38, 39]. This type of stabilizing system can give rise to some type of nanocomposite material since the organic layers form a Nanometric scale second phase. These stabilization types are illustrated in Scheme 1.
Scheme 1. Schematic representation of the electrostatic and steric stabilization in metal NPs.

Due to their properties cited above, ionic liquids can be an alternative to such ligand layers without adding any additional stabilizer, surfactants or capping ligands [40-42].

Most of the studies deal with a parallel and synergistic development of both nanoparticles and ionic liquids for materials chemistry [43], whereas other are devoted to the study of the dispersion of inorganic nanoparticles in ionic liquids [44]. In light of the various associations mentioned before, it will be shown how such hybrid gold nanoparticle/imidazolium compounds can be considered as new highly promising materials.

The optical properties of gold nanoparticles are dominated by surface plasmon resonance induced by light irradiation. The surface plasmons absorption originated from the interaction of external electromagnetic radiation with highly polarizable Au 5d10 of Au nanoparticles [45]. (Scheme 3)

Scheme 2. Origin of surface Plasmon resonance due to the coherent interaction of the electrons in the conduction band with the electromagnetic field.

The optical absorption spectrum shows a surface plasmon resonance (SPR) band at 550nm Figure 1 indicating that it is in a metallic state.
Figure 1. The UV-Visible absorption spectra of gold nanoparticles

Figure 2. shows the photoluminescence (PL) of gold metallic NPs, the emission spectra is characterized by the presence of one sharp peak in the red-band region showing the fundamental absorption of gold nanoparticles with the peak center at nm 426 nm attributed to quantum confinement of electrons from gold nanoparticles. The excitation spectrum is observed with a sharp and intense peak centered at 310nm.

Figure 2. The fluorescence spectra of gold nanoparticles, Excitation spectra (dashed curve) and the emission spectra (solid curve)

The observed PL from this sample is due to electron-hole recombination that occurs between the excited electrons near the Fermi surface and holes in the d band [46]. The outermost d and s electrons of the
constituent atoms must be treated together leading to 6 bands. Five of them are relatively flat, lying a few eV below the Fermi level, they are usually denoted as d bands; the 6th one, which is almost free-electron like is known as the conduction band or sp band. A sketch of a possible transition occurring in the quantum dots related to the fluorescence is given in Scheme 3.

**Scheme 3.** The possible transition is occurring in the Au quantum dots.

The gold nanoparticles, used as supplied are dispersed in ionic liquid emim BF$_4$. This procedure has no effect on the gold nanoparticles core shape or size. After adding the gold nanoparticles to the emim BF$_4$ solution, the reaction pot was directly immersed in an ultrasonic bath and kept under sonication for 2 hours.

Characterization by TEM and UV-Vis spectroscopy of the Au-emim BF$_4$ was performed to evaluate the preservation of the morphology and optical properties of colloidal nanostructures after fusion with emim BF$_4$. 
Figure 3. UV-Vis absorption spectra. Bare Au Nanoparticles (black), Au NPs + emim BF$_4$ (red)

Figure 3, shows the absorption spectrum of the Au-emim BF$_4$. The characteristic absorption spectrum of the gold nanoparticles dispersed in emim BF$_4$ attest to the presence of both inorganic gold nanoparticles and the emim BF$_4$ components in the UV spectral region. The absorption peaks appeared red shifted in the range of 438-560 due mainly to the influence of the $\pi$-$\pi^*$ transition of the imidazolium ring. As the plasmon absorption of gold nanoparticles is sensitive to the surrounding environment, the observed weak absorption and the absence of the usual bell-shaped band of the gold plasmon resonance might be attributed to the formation of bonded ionic liquid layer. The subsequent increase of the ionic liquid field on the surface of Au NPs, in other words is due to the weak surface plasmon resonance (SPR) of the gold nanoparticles embedded in ionic liquid medium. The tail which instead appear in the spectra of Au-emim BF$_4$ in the visible range, can be ascribed to the presence of energetically different associated structures, originating from an interaction among the $\pi$ delocalized orbital of the imidazolium ring. Note that the intensity of the absorption was increased by a fold in the blue region. This tail probably due to the monomeric form of imidazolium ion free ion and has nothing to do with the composite [47, 48].

Useful information on the surface modification of gold nanoparticles was also obtained from photoluminescence spectra Figure 4.
By comparing to Au, emission spectra of emim BF₄-Au mixture exhibit a new shoulder peak at 438 nm, which may be attributed to the excimer emission of π-π interaction between the free imidazolium moieties. This is confirmed in the PL emission of blank emim BF₄, which shows the same shoulder at the same position meaning that it is not coming from ionic liquid surrounding the gold nanoparticles. Moreover, the small shift of the emission maximum toward longer wavelength suggests the existence of string π-π stacking in the medium. The maximum of the band-edge PL emission of fusion material is weakly shifted, confirming that the capping exchanges does not modify the geometrical properties of the Au NPs. The increase in the absorption intensity is due to the contribution from the emim BF₄ as a consequence of the transition of the π* excited state to the π energy level in the aromatic ring [47, 48]. The broad emission of the nanocomposite is due to hierarchical stacking of the imidazolium structures around the particles which would influence the band.

The morphology of the dispersed gold nanoparticles was investigated by direct observation using in situ TEM (Figure 5.), which is possible in the ionic liquid medium despite the high vacuum condition and the high energy of the electron beam. TEM was performed on samples prepared using the Au-emim BF₄ suspension ultrasonically dispersed and then deposited on holey carbon film supported on a copper grid; the grid was placed on filter paper to remove the excess material and was allowed to dry under vacuum. The solution contains particles with a uniform size of 50 nm. The micrographs in figure 4 also show that gold nanoparticles are well dispersed in the ionic liquid, but some of them aggregate into larger blobs. As can be seen from the illustration 4b, the ligne profile analysis shows a distinct surface layer of the ionic liquid emim BF₄ around the Au-NPs.

**Figure 4.** PL emission spectra. (a) Neatemim BF₄ (b) Au nanoparticles (c) Au ‘‘NPs’’ + emim BF₄
The presence of the IL around the NPs was confirmed by the time-resolved PL decay curves for Au and Au NPs in emim BF$_4$ at the emission wavelength peak of 310 nm. Emim BF$_4$ ionic liquid surrounding the nanoparticle surface act as effective stabilizers of Au nanoparticles which will reduce the average lifetime, in the Au-emim BF$_4$(2.74 ns) compared to pure IL(4.69 ns). This reduction in the transition lifetime indicates clearly that the charge transfer process is occurring from emim BF$_4$ to Au nanoparticles.

![Figure 5. Typical TEM micrograph and ligne profile of Au nanoparticles](Image)

**Figure 5.** Typical TEM micrograph and ligne profile of Au nanoparticles

The ionic liquid precursor emim BF$_4$ as shown below played a significant role in the stabilization of metallic nanoparticles. The stabilization of gold nanoparticles in the ionic liquid is better explained using the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [49, 50], which treat the IL ions as point charges, providing an electrostatic protection by the formation of ‘’protective’’ anionic and cationic layers ‘’shells’’ around the NPs in core shell system. IL network should be considered as supramolecular polymeric structures with high degree of self-organization and weak interactions that bind weakly to the metal surface than to other anions or capping ligands [31]. When mixed with metallic nanoparticles IL becomes organized and nanostructured with two regions: polar and a nonpolar one [51-54]. Based on the above results and in accordance to DLVO theory gold nanoparticles are considered to be stabilized by the BF$_4^-$ anion and large

![Figure 6. Lifetime decay of the IL and IL+ Au nanoparticles at 426 nm emission wavelength](Image)

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imidazolium cation, firstly by the formation of anionic BF$_4^-$ shell as first inner shell, the Au/BF$_4^-$ layer is expectedly surrounded by imidazolium cations (Scheme 4).

![Scheme 4](image-url)

**Scheme 4.** Schématique représentation of structural organization of Au-emim BF$_4$ IL.

### 3. Conclusion

The interaction between Au-NPs and imidazolium IL in a uniform hybrid material resulting from fusion of luminescent Au-NPs in emim BF$_4$ ionic liquid has been studied as model compound using spectroscopic and morphological techniques. From the result obtained by steady state spectroscopy as well as time-resolved spectroscopy and TEM micrographs show the existence of a layer of the IL on the Au-NPs surface via weak parallel coordination, due to an electrostatic stabilization. On the other hand Imidazolium moiety act as cationic barrier inducing steric stabilization avoiding further aggregation of Au NPs.

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