Synergistic response of ionic liquid (bmimBF₄) entrapped in BHDC reverse micelles for gold nanoparticles synthesis. Size and morphology control

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ABSTRACT

Herein, we reported the effect of toluene/benzyl-n-hexadecyldimethylammonium chloride (BHDC)/1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄) RMs as nanoreactor for gold nanoparticles (AuNPs) synthesis, we evaluated the effect of IL and the confinement on the kinetic AuNP_S formation, its size and morphology. The results are compared to those obatined in neat IL and in analogous aqueous RMs media. The resuls showed that besides the ILs supramolecular network, the confinement plays an importan roll on the kinetic AuNPs formation. Is known in RMs the interaction between polar solvent (bmimBF₄ and water) and BHDC interface are different, hence the interface properties shuch a fluidity are also modified. The results indicates the fluidity of [bmim][BF₄]/BHDC/toluene interface encourage by IL, enhance the material exchange between droplets induced a simple kinetic and the formation of larger AuNPs in comparison to those formed in aqueous RMs.

Keywords: reverse micelles, ionic liquids, novel reaction media, gold nanoparticles.

1. INTRODUCTION

The design and preparation of metal nanoparticles (M-NPs) have recently been the center of great attention due to their important applications.[1, 2] M-NPs with specific chemical, physical, and electronic properties can be attained by manipulating the particle size and morphology. Reverse micelles (RMs), has been demonstrated as a very versatile and reproducible method successfully used to prepare wide variety of nanoparticles with different chemical nature, size and shape.[3, 4].

RMs are spatially ordered macromolecular assemblies of surfactants formed in a nonpolar solvent, in which the polar head groups of the surfactants point inward and the hydrocarbon chains point toward the nonpolar medium.[5] The water pools of the RMs act as nanoreactors which efficiently mix the reactants and form the NPs, and the surrounding surfactant layer limits their growth and protects them from aggregation. [6]

Most of phenomena and properties of RMs have the origin in the droplet-droplet interaction, thus, the composition of RMs is a fundamental fact that impact on the droplet size, the fluidity of interface, and the interaction between droplet.[7, 8] In this sense the synthesis of NPs using RMs as nanoreactors is viable and attractive because it does not only produce nanoparticles that have a narrow size distribution, but also the particle morphology can be controlled by varying the microemulsion composition [9, 10].

There are a wide range of surfactants that form RMs in both the presence and absence of cosurfactants.[5, 11] One of them, the cationic surfactant, benzyl-n-hexadecyldimethylammonium chloride (BHDC, Scheme 1), can form RMs in aromatic solvents without addition of a cosurfactant.[8, 12, 13] Although the traditional solvent used as polar component in BHDC RMs is water, different polar solvent, for example ILs [14-18] can be entrapped in the polar core.
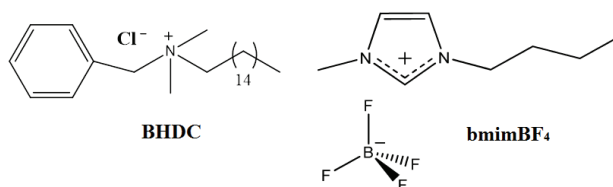
Scheme 1. Molecular Structures of BHDC and bmimBF4

Ionic liquids are unique alternatives to traditional aqueous or organic solvents. [19, 20] [21] and they have been used successfully as reaction media for M-NPs synthesis since their electrostatic and steric ("electrosteric") properties can stabilize M-NPs without any aditional stabilizer.[22, 23]

Recent studies have showed that the physicochemical properties of polar solvents (including ILs) entrapped inside RMs change dramatically from those of the bulk solvents as a result of specific interactions and confined geometries. 4,12 Whether altering physicochemical properties of ILs inside RMs affects solute species as reactants and the course of reactions remains to be explored.[17] Actually, these RM systems formed utilizing ILs as polar components are very attractive.[18] These IL RMs have gained attention because of their potential applications owing to the unique features of both ILs and RMs. The RMs provide hydrophobic or hydrophilic nanodomains, thereby expanding the potential uses of ILs in chemical reactions, allowing the use of smaller quantities of IL compared to that required for bulkphase ILs reactions.[20, 24]

In this sense, our aim is to evaluated the synergistic response of bmimBF$_4$ entrapped in toluene/BHDC RMs as nanoreactor for gold nanoparticles (AuNPs) synthesis, we pretend to understand how the propeties of bmimBF$_4$ under confinent are reflected on the size and morphology of the AuNPs synthetized. We compared the resuts obtained using this nonaqueous system to those obtained in neat bmimBF$_4$ and in aqueous RMs media.

For AuNPs synthesis a typical RMs methodology was used, where A and B RMs interact and the reduction process take place because of the exchange process.[4] We used tetrachloroauric acid (HAuCl$_4$) as precursor and hydrazine (N$_2$H$_4$) as reducing agents.

2. EXPERIMENTAL SECTION

2.1. Materials

Toluene from Sigma (HPLC quality), was used without prior purification. The surfactant Benzyl-n-hexadecyldimethylammonium chloride (BHDC), from Sigma (> 99% purity) and the IL 1- butyl-3-methylimidazolium tetrafluoroborate (bmimBF$_4$) from Sigma-Adrich (BASF quality, >98%). were used as received, and to minimize water absorption, they were kept under vacuum. Ultrapure water was obtained from Milli-Q equipment. Tetrachloroauric acid (HAuCl$_4$, Sigma-Aldrich) as precursor, and hydrazine monohydrate (N$_2$H$_4$.H$_2$O, Sigma-Aldrich) and sodium borohydride (NaBH$_4$, AppliChem) as reducing agents for gold nanoparticles synthesis were used as received.

2.2 Methods

Stock solutions of BHDC in toluene were prepared by mass and volumetric dilution to obtain optically clear solutions, bmimBF$_4$ or water was added using a calibrated microsyringe. The incorporation of polar solvents into each micellar solution was performed using calibrated microsyringes. The amount of water or IL present in the system is expressed as the molar ratio between polar solvent and the surfactant W_0= [water]/[BHDC] and W_s = [IL]/[BHDC]. All experimental points were measured three times with different prepared samples. The pooled standard deviation was less than 5%. In all the cases, the temperature was kept at 25 °C ± 0.2 °C. It is important to note that, at room temperature, bmimBF$_4$ or water are not soluble in toluene or in toluene/BHDC solutions at surfactant concentrations lower than the critical micelle concentration (cmc; around 0.01 M).[25]

The methodology used to synthesize AuNPs in RMs is based on mixing two identical RMs, each containing one of the reactants (tetrachloroauric acid and hydrazine) these RMs interact and the auric ions are reduced to nucleation and growth in a limited space (polar core).[4] For example, a solution of toluene/BHDC RMs ([BHDC] = 0.1 M) containing tetrachloroauric acid dissolved in water (0,05M) at W_0 = 5, and another containing hydrazine (0.3 M) dissolved in water at the same BHDC concentration

and W_0 were prepared. The reduction process takes place when the two BHDC RMs systems are mixed by magnetic agitation at room temperature. The same procedure was used for nonaqueous RMs, in this case the reactants are dissolved in bmimBF$_4$ instead of water, and the W_s evaluated was W_s = 0,8.

2.3 General

UV/visible spectra were recorded using a spectrophotometer Hewlett Packard-Agilent 8453 with a thermostated sample holder. The path length used in all experiments was 1 cm.

The micrographs were recorded using a Transmission Electron Microscopy (TEM) FEI TECNAI G2 STWIN with a camera Gatan ES100W and software Gatan Digital Micrograph. For TEM studies, the samples were placed into a formvar-covered copper grid.

3. RESULTS AND DISCUSSION

3.1. AuNPs sythetized in neat IL bmimBF$_4$

In general, the reduction of metal salts is the most utilized method to generate M-NPs in ILs, several different M-NPs have been prepared. [23] However, there isn´t reports about AuNPs synthesis in bmimBF$_4$ using hydrazine a weak reducing agent. Figure 1A shows the kinetic of AuNPs formation in neat bmimBF$_4$
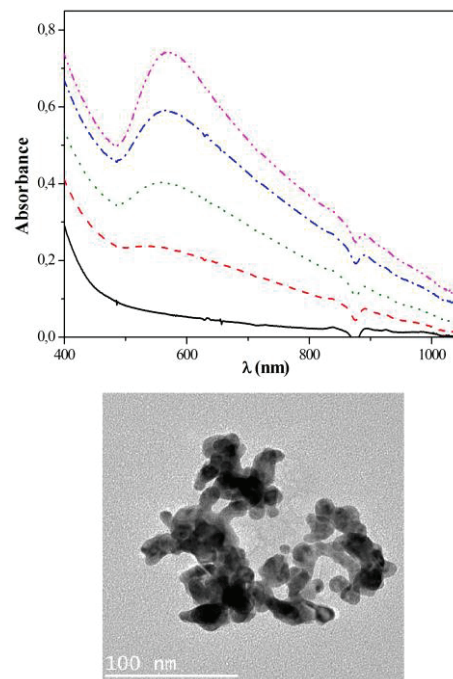

Figure 1. Absorption spectra as a function of reaction time for AuNPs synthetized in neat bmimBF$_4$. Time (sec) = 0 (—), 30 (– – –), 60 (· · ·), 90 (– · –), 180 (– · · –), and TEM micrograph. [HAuCl$_4$] = 8E-4 M y [N$_2$H$_4$] = 5E-3 M dissolved in bmimBF$_4$ was used as precursors. BmimBF$_4$ neat was used as blank.

In an attemp to understand the formation mechanism of the AuNPs in different reaction media, we consider the growth kinetics as the key point in determining the final NPs morphology. For example, in neat bmimBF$_4$ an homogeneous media (Figure 1) an unique broad band (λmax= 568 nm) is observed, increasing its intensity as particles grow. The complete reduction of gold take place after 180 seconds, then the localized surface plasmon resonance (LSPR) remains constant. Those results suggested bmimBF$_4$ favors the interactions between NPs resulting in particles with not much defined morphology. As can be observed, TEM micrograph support the initial kinetic information, the images showed that AuNPs obtained in neat bmimBF$_4$ are stable aggregates arround 50 ± 10 nm of size. In this sense it is possible to say that the supramolecular ionic liquid network does supplie the

necessary electrostatic and steric stabilization [26, 27], but it does not control the morphology or size.

3.2. AuNPs in nonaqueous and aqueous toluene/BHDC RMs

RMs as nanoreactors has been demonstrated as a very versatile and reproducible method used to prepare nanoparticles.[3, 4]. Despite of aqueous RMs are the most studied systems, nonoaqueous RMs represent a promising media for NPs synthesis due their unique properties.[5] To the best of our knowledge, this is the first time where toluene/BHDC/bmimBF$_4$ system is used as nanoreactors for AuNPs synthesis. Figure 2 shows the spectra of kinetic AuNPs formation in toluene/BHDC/bmimBF$_4$ and in toluene/BHDC/water RMs.
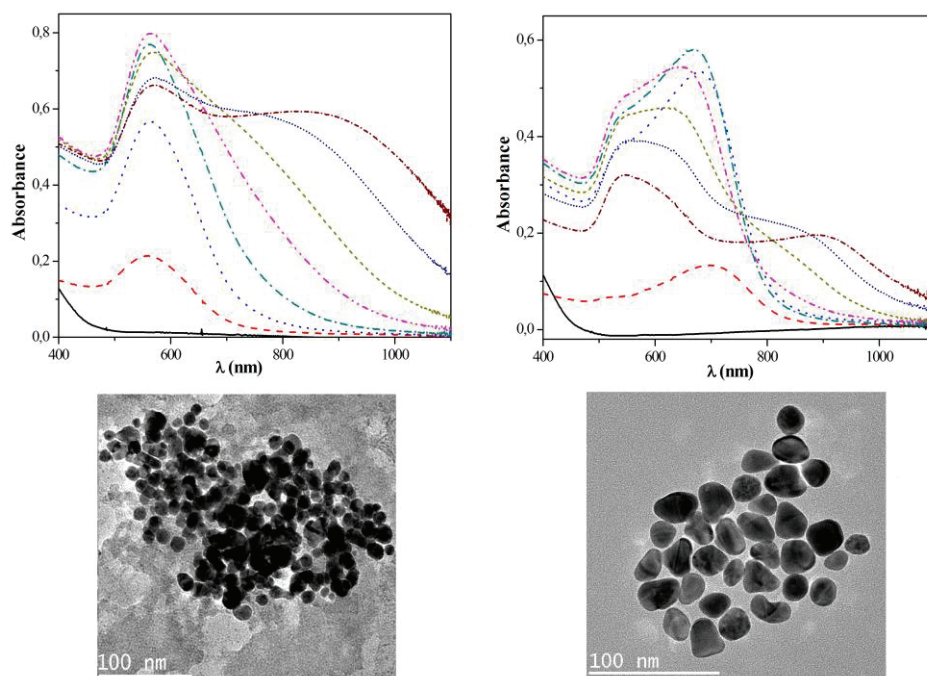

Figure 2. Absorption spectra as a function of reaction time for AuNPs synthetized in A). Toluene/BHDC/bmimBF$_4$ at W$_s$ = 0.8, and B.) Toluene/BHDC/water at W$_0$ = 5. Time (min) = 0 (—), 1 (– – –), 2 (· · ·), 3 (– · –), 4 (– · · –), 5 (----), 6 (····) and 7 (-·-·-), and TEM micrograph. [HAuCl$_4$] = 0,05M y [N$_2$H$_4$] = 0,3M dissolved in bmimBF$_4$ and water respectively was used as precursors. BHDC RMs without addition of polar solvent was used as blank.

As can be seen in Figure 2, The polar solvent entrapped in RMs strong influences the kinetic AuNPs formation. In Figure 2A where bmimBF$_4$ is entrapped an initial band centred at λmax= 570 nm is observed, this high energy band increases its intensity through the time suggesting the initial formation of small particles. When the reaction proceed the high energy band decreases its intensity and an important lower energy band arises, finally after 7 minutes of reaction the spectrum remains constant with the presences of two absorption maxima at λmax= 570 and 870 nm. This kind of kinetic in general indicated an

anisotropic NPs growth [28, 29]. TEM micrograph as well as kinetic information shown anisotropic small and isolated particles of 15 ± 3 nm. In Figure 2B when water is entrapped, similar result was obtained despite of the kinetic AuNPs formation developed in a different way, in this case an initial broad band centred at λmax= 705 nm is observed, this band suddenly increases its intensity and small shoulder at high energy (λmax= 540 nm) appears, interestingly through the time the initial band desapears, bring on the shoulder in an important band and the developed of a new band at lower energy (λmax= 905 nm).

Finally as in toluene/BHDC/bmimBF$_4$ RMs after 7 minutes of reaction the spectrum remains constant with the presences of two absorption maxima in this case at λmax= 540 and 905 nm.TEM micrograph obtained for the final reaction products in this system showed anisotropic small and isolated particles of 23 ± 2 nm.

The results from neat bmimBF$_4$ in comparison to those obtained in bmimBF$_4$ under confiment, demostrate the synergistic response of this RMs system as nanoreactor for AuNPs synthesis, as was observed when IL is entraped is possible to form anisotropic particles controlling size and morphology complete different from those obtained in homogeaneos media (neat bmimBF$_4$).

In RMs system the result shown the effect of the polar solvent entrapped on the RMs properties, as was perviously mantionated, the composition of RMs is a fundamental fact that impact on the droplet interaction and influences the final product.[7] Previous reports demostrated a strong interaction between IL and BHDC interface in toluene/BHDC/bmimBF$_4$ RMs [14, 16] Aparently, these ions segregation enhaced the interface fluidity therefore droplet-droplet interaction. The RMs interaction favors the fast reduction of gold ions and the formation of much and small NPs[7] as was observed in TEM images. From result in toluene/BHDC/water RMs is possible to suggest the interface of this sistem is less fluidity from observed in toluene/BHDC/bmimBF$_4$ RMs therefore the results shown less quantity and biggers NPs.

4. CONCLUSIONS

This is the first time where toluene/BHDC/bmimBF$_4$ RMs are used as nanoreactors for AuNPs synthesis. The results show the versatility of this system to synthetized anisotropic AuNPs controlling size and morphology, we demostrate the synergistic response of this RMs system as nanoreactor in comparison to neat bmimBF$_4$ media. We demostrated by AuNPs synthesis the effect of polar solvent entrapped on the RMs properties, we found IL enanced the interface fluidity in comparison to water, favours the formation of more and smaler anisotropic AuNPs.

ACKNOWLEDGMENTS

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