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ORIGINAL ARTICLE

Synthesis of biologically stable gold nanoparticles using imidazolium-based amino acid ionic liquids

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Abstract A novel double-step reduction procedure for the synthesis of gold nanoparticles (AuNPs) using amino acid ionic liquids has been employed. 1-Dodecyl-3-methyl imidazolium tryptophan ([C_{12}mim]Trp) and 1-ethyl-3-methyl imidazolium tryptophan ([C_2mim]Trp) were used for this synthesis. The synthesized AuNPs were characterized by UV–vis spectroscopy, transmission electron microscopy and dynamic light scattering. The behavior of these AuNPs were also probed in a biological media. It was proven that AuNPs synthesized at [C_{12}mim]Trp have more stability than AuNPs synthesized at [C_2mim]Trp due to the longer alkyl chain of the imidazolium moiety. The solubility test shows that the resultant AuNPs have a hydrophilic nature. Finally, it was seen that due to the presence of a biomolecule, namely Trp, in the structure of AuNPs protecting shell, higher stability and biocompatibility was achieved in the biological media.

Keywords Gold nanoparticle · Amino acid ionic liquid · Tryptophan · Double-step reduction · Biological stability

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Introduction

The fascinating quantum size effects attributed to nanoparticles (NPs), have made them applicable to different areas such as photonics, microelectronics, nano scale sensors, detection systems, sensing, agricultural area, medicine, catalysis, etc. (Jain et al. 2007; Miranda et al. 2010; Katz and Willner 2004; P'erez-Juste et al. 2005; De et al. 2008; Agasti et al. 2010). The applicability of the NPs is determined by a set of physicochemical parameters that may include their size, shape, structure, central core composition, and surface functionalities. Therefore, one should pay attention to all of the above factors in the synthesis step in order to achieve the desired functionality. There have already been rapid progresses in designing NPs with different practical characteristics (Xia et al. 2009). However, as the science continues its surveys, there are still necessities for fabrication and modification of NPs to achieve the deliberate functionality for novel applications.

Among all metal NPs, gold nanoparticles (AuNPs), particularly, have a brilliant history in chemistry (Daniel and Astruc 2004; Eustis and El-Sayed 2006). AuNPs are the first choice for biological applications since gold has no toxicity or the so called "inherent bioinertness" (Giljohann et al. 2010). This is the reason of its wide applications in biology and medicine including gene and drug delivery applications, biodetection and biodiagnostics, bioelectronics and sensing applications (Ghosh et al. 2008; De et al. 2008). Not only this bioinertness property is a great advantage of AuNPs, but also affinity of gold itself, toward functional groups such as thiols, phosphines and amines is very attractive. In this way, AuNPs can be functionalized using a modified capping agent containing one of these functional groups. Furthermore, AuNP surface can be easily decorated with the desired biomolecules such as

oligonucleotides, proteins or drugs, attached to one of these functional groups (You et al. 2006; Ghosh et al. 2008).

Ionic liquids (ILs) are among the most attractive class of substances in chemistry. They have attracted a great deal of attention because of inherent unique physicochemical properties including negligible vapor pressure, nonflammability, low toxicity, high chemical and thermal stability, controllable hydrophobicity and good conductivity. Their distinctive properties have lead to widespread use as green solvent in organic synthesis (Marsh et al. 2002), electrochemistry (Maleki et al. 2006), separation science (Absalan et al. 2010; Berthod et al. 2008), medicine (Malhotra and Kumar 2010), delivery applications (Zhang et al. 2009; Dobbs et al. 2009) and even NP synthesis (Li et al. 2005; Ren et al. 2008; Zhang and Cui 2009; Singh et al. 2009; Itoh et al. 2004; Shan et al. 2008; Safavi and Zeinali 2010). Imidazoilum based ILs, among others, show preferential binding affinity toward gold crystal surface in the synthesis of AuNPs (Safavi and Zeinali 2010) and have also low cytotoxicity and high biocompatibility in biomedical applications (Cho et al. 2007; Romero et al. 2008; Kumar et al. 2009).

In this work, a new class of functionalized AuNPs have been synthesized using imidazolium-based ionic liquids containing tryptophan (Trp) amino acid molecule: 1-dodecyl-3-methyl imidazolium tryptophan ([C_{12}mim]Trp) and 1-ethyl-3-methyl imidazolium tryptophan ([C_2mim]Trp) (Wu and Zhang 2009; Fukumoto et al. 2005; Peng et al. 2009; Ohno and Fukumoto 2007). Amino acids, themselves, have been widely used in the synthesis of AuNPs (Selvakannan et al. 2004a; Mandal et al. 2002; Selvakannan et al. 2003; Shao et al. 2004; Kasture et al. 2010; Selvakannan et al. 2004b; Bhargava et al. 2005). Some of these amino acids such as tryptophan, aspartic acid and tyrosine have been also used as a reducing agent. Because Trp produces water dispersible AuNPs upon reduction (Selvakannan et al. 2004a), a double-step reduction procedure is used here to produce water soluble AuNPs. First, gold ions were reduced by Trp. Then the reduction of AuNPs were continued using a strong reducing agent namely sodium borohydride ($NaBH_4$). By this methodology, the dispersed AuNPs produced by the reduction of Trp, in the first step, is transformed to the soluble ones, in the second step.

The motivation for synthesis of these AuNPs was to introduce a potential gene delivery vector. Imidazolium backbones are efficient gene delivery vectors (Midoux et al. 2009). They can electrostatically interact with the negative backbone of DNA due to their positive charge. Therefore, functionalizing AuNPs with ILs containing an amino acid, as a biomolecule, and an imidazolium moiety, which has high binding affinity toward DNA along with low toxicity (Romero et al. 2008; Cho et al. 2007; Kumar et al. 2009), seems to be a satisfactory combination. It is necessary to mention that not only the advantage of imidazolium moiety of the IL was our goal, but also that of Trp moiety, since Trp is a biocompatible molecule (Zhang et al. 2009).

A comparison between AuNPs stabilized at [C_{12}mim]Br, (AuNP@[C_{12}mim]Br) (Safavi and Zeinali 2010) and the newly synthesized NPs (AuNP@[C_{12}mim]Trp and AuNP@[C_2mim]Trp) has also been carried out in order to check the difference in their behavior upon substitution of Trp by halogen molecules.

Experimental

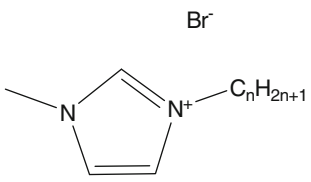
Materials

Tetrachloroauric acid ($HAuCl_4$), sodium borohydride ($NaBH_4$), 1-methylimidazole, 1-bromoethane, 1-bromododecane, tryptophan (Trp), diethyl ether, tetrahydrofuran (THF), potassium hydroxide, Amberlite IRA-400 (OH) was purchased from Merck. All reagents were used as received without further purification.

Amino acid ionic liquid synthesis

Synthesis of [$C_n$mim][Br] ($n = 2, 12$)

The first step toward the synthesis of amino acid ionic liquids (AAILs) is the synthesis of halogenated ILs [$C_n$mim][Br] ($n = 2, 12$). 1-Ethyl-3-methyl imidazolium bromide and 1-dodecyl-3-methyl imidazolium bromide were synthesized according to a standard procedure (Wasserscheid and Welton 2008) by the reaction of 1-methylimidazole with slight molar excess of 1-bromoethane and 1-bromododecane. The reactants were stirred without addition of any solvent for 72 h. Heating at 70°C and refluxing was necessary in the case of $n = 12$. The [$C_n$mim][Br] products were then purified by repeated rinsing with diethyl ether following drying under vacuum conditions. All the products were characterized with ^{1}HNMR. The structure of the synthesized ILs is presented in Scheme 1.



Scheme 1 Structure of the synthesized ILs: 1-dodecyl-3-methyl imidazolium bromide ($n = 12$); 1-ethyl-3-methyl imidazolium bromide ($n = 2$)

Synthesis of [$C_n$mim][Trp] ($n = 2, 12$)

Synthesis of AAILs was performed in two steps according to previous reported procedures (Peng et al. 2009; Fukumoto et al. 2005).

1. Synthesis of [$C_n$mim][OH] from [$C_n$mim][Br]

[$C_n$mim][Br] was added to an excess amount of KOH in the presence of dry THF in an Erlenmeyer flask equipped with a drying tube. The mixture was then subjected to sonication in an ultrasonic clean bath for 2 days. After allowing the reaction container to stand overnight, it was filtered through a sintered funnel. The filtrate was concentrated under vacuum until the viscous liquid of [$C_n$mim]OH was obtained. In order to remove residual halide, Amberlite IRA-400 (OH) anion exchange resin was used. At last, acid–base titration was used to determine the concentration of the product.

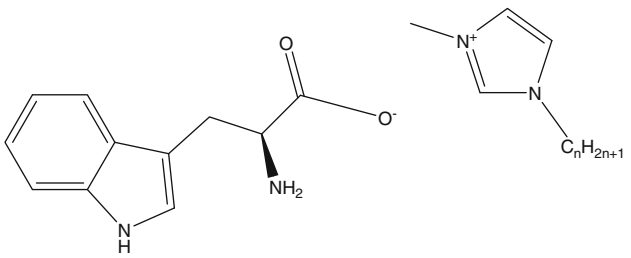
2. Synthesis of [$C_n$mim][Trp] from [$C_n$mim][OH]

[$C_n$mim][OH] aqueous solution was added to a slight molar excess of Trp aqueous solution and was stirred for 24 h. After evaporation of water under vacuum conditions at 40–50°C, acetonitrile–methanol mixture (9:1) was added to the vessel and stirred vigorously. By filtering this mixture, the excess Trp was removed. Finally, after evaporation of the solvent, and drying in vacuum for 2 days at 80°C, the structures were characterized with ^{1}HNMR. The structure of the ILs used in AuNP synthesis is presented in Scheme 2.

Synthesis of AAIL-protected gold nanoparticles

Our study revealed that a double-step reduction methodology can produce water soluble AuNPs with small sizes.

In the first reduction step, Trp (in the AAIL structure) reduces the gold ions and acts as a capping agent, as well. The resultant AuNPs are water dispersible. In the second reduction step, a solution of $NaBH_4$ (a strong reducer) was added to the NPs which resulted in water soluble NPs. The exact procedure is as follows.



Scheme 2 Structure of the AAILs used for the synthesis of AuNPs ($n = 2, 12$)

200 μL of 0.005 M aqueous solution of $HAuCl_4$ was added to 5 ml of AAIL under mild heating at 50°C while stirring vigorously. It has been proved that the rate of reduction of gold ions by Trp is considerably enhanced at 50°C (Selvakannan et al. 2004a). Hence, all AuNPs were synthesized at this temperature. When water dispersible AuNPs were synthesized in the solution, the color turned reddish. In this stage, freshly prepared 0.4 M $NaBH_4$ aqueous solution was added dropwise until the dispersible AuNPs became soluble with a shinny color.

In order to achieve the finest AuNPs with high stability, the mole fraction (R) of the precursors (AAILs to the gold ions) should be optimized with respect to each other. Optimization experiment was arranged for the R values of 0.75, 1.5, 3.0, 4.5, 6.0, 7.5, 9.0, and 10.5 in which the final concentration of AAIL was 1.44×10^{-4}, 2.884×10^{-4}, 5.769×10^{-4}, 8.653×10^{-4}, 1.154×10^{-3}, 1.44×10^{-3}, 1.73×10^{-3} and 2.02×10^{-3} M, respectively.

Instrumentation

A Schimadzu spectrophotometer was used for recording the UV–vis spectra of the AAIL-protected AuNPs using a 1 cm quartz cell. Dynamic light scattering (DLS) measurements were performed with a HORIBA L-550 at a fixed scattering angle of 90° and at a constant temperature of 25°C. Transmission electron microscope (TEM), Philips CM10, operated at an accelerating voltage of 100 kV was used to obtain the TEM micrographs of the AuNPs.

Results and discussion

Optimization experiment and UV–vis measurements

Surface plasmon resonance (SPR) band along with color changes in solution were used as good indicators for the synthesis of the desired AuNPs under the optimum conditions.

The SPR changes of AuNP@[C_{12}mim][Trp] at different mole fractions (R) are shown in Fig. 1. The inset shows their corresponding solution color. The data revealed that the optimum mole fraction for the synthesis of AuNP@[C_{12}mim][Trp] is $R = 3$. This is observable from the change in color from purple to red and the SPR variations. It has been proved that SPR is strongly dependent on the closeness of NPs to each other (Su et al. 2003). Therefore, aggregation of AuNPs result in a red to blue shift accompanied with broadening of SPR band. Hence, when the mole fraction of [C_{12}mim][Trp] to

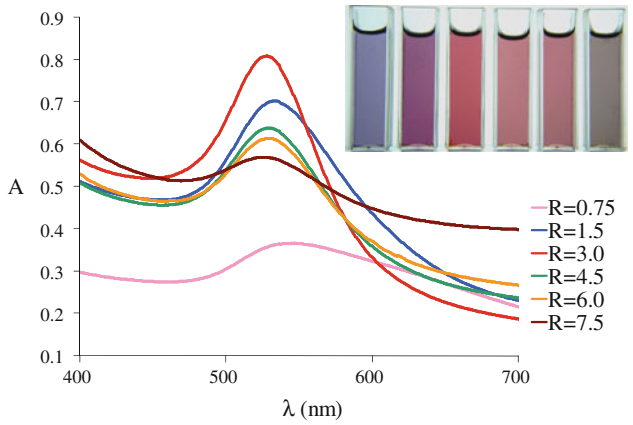


Fig. 1 UV–vis spectral changes of AuNP@[C_{12}mim]Trp by increasing AAIL concentration. The inset shows the accompanying change in color (from *left* to *right* $R = 0.75, 1.5, 3.0, 4.5, 6.0, 7.5$)

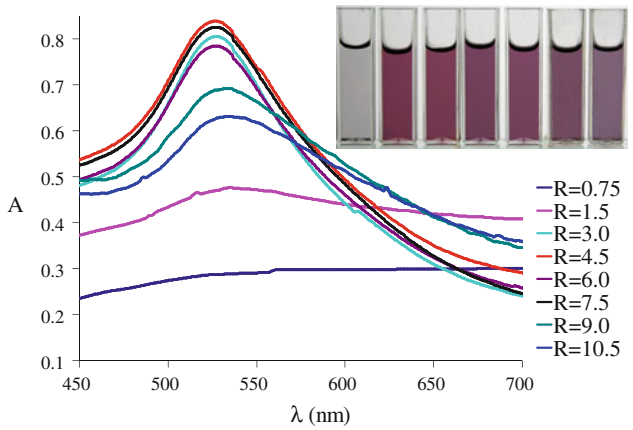


Fig. 2 UV–vis spectral changes of AuNP@[C_2mim]Trp by increasing AAIL concentration. The inset shows the accompanying change in color (from *left* to *right* $R = 1.5, 3.0, 4.5, 6.0, 7.5, 9.0, 10.5$)

gold ions is three ($R = 3$), the amount of capping agent is sufficient to produce monodispersed AuNPs.

It is believed that upon reduction of gold ions with Trp, its indole ring is oxidized to oxindole. This oxidation is accompanied by some degree of polymerization and consequently led to cross-linking in AuNPs (Selvakannan et al. 2004a). It seems that the produced AuNPs get stock in the invisible polymerization cluster. Addition of $NaBH_4$ to the reduced AuNPs by Trp, breaks this cross linking to an acceptable degree and consequently produces water soluble AuNPs.

Figure 2 shows the SPR changes of AuNP@[C_2mim][Trp]. Since Trp can act as a capping agent itself, AuNP@[C_2mim]Trp was synthesized to study any stabilization effect that could be induced by the alkyl chain length in AuNP@[C_{12}mim]Trp.

Clear differences can be observed between the sharpness of the SPR bands and also the color of AuNP@[C_{12}mim]Trp and AuNP@[C_2mim]Trp. The best mole fraction for the synthesized AuNP@[C_2mim]Trp was $R = 4.5$ while that of AuNP@[C_{12}mim]Trp was $R = 3$. Therefore, higher concentrations of [C_2mim]Trp is needed to have the most stable AuNPs. Moreover, the dull color of AuNPs@[C_2mim]Trp could be due to the coupling in oscillation of surface plasmon electrons as a result of inter-particle interactions. Thus, it can be concluded that the long alkyl chain of AAILs leads to lower aggregation, higher stability and dispersibility of AuNPs.

TEM and DLS analysis

Figure 3 shows the TEM images of AuNP@[C_{12}mim]Trp and AuNP@[C_2mim]Trp.

More dispersible NPs are obtained when [C_{12}mim]Trp was used as the capping agent and this could only be the effect of alkyl chain length that provides a longer distance for the neighboring NPs (Scheme 3).

Particle size distribution graphs (Fig. 4) are in agreement with TEM images and demonstrate the distribution range of AuNPs. In addition, higher dimensions of NPs protected by [C_2mim]Trp is evidenced from these graphs.

Solubility test

A solubility test was performed to investigate the hydrophilic behavior of the as-prepared AuNPs. As mentioned earlier, the behavior of AuNP@[C_{12}mim]Br was also monitored to study the anion effect. To do so, about 2 ml of the as-prepared AuNPs (which are in aqueous media) was added to about 5 ml of the following organic solvents (*N*-hexane, chloroform, dichlorometane, THF) and was stirred vigorously. In the case of hydrophobic solvents (*N*-hexane, chloroform and dichlorometane), the NPs did not enter the organic phase. On the other hand, complete solubility was observed in the case of THF, as a polar hydrophilic solvent. This result arises from the hydrophilic nature of the as-prepared NPs which could be exerted by the ionic part of the molecule; imidazolium ring and zwitter ionic characteristic of amino acid moiety.

Stability test

The behavior of the synthesized AuNPs was monitored under different conditions to investigate their stability. To do so, the changes in their SPR band were recorded. The more stable the AuNP, the less shift in the SPR band should be observed. This stability or shift reveals the strength of the NPs' protecting shell or else the capping agent. If the NPs show instability under a certain condition, they will aggregate and it causes a broadening and shift in the SPR band.

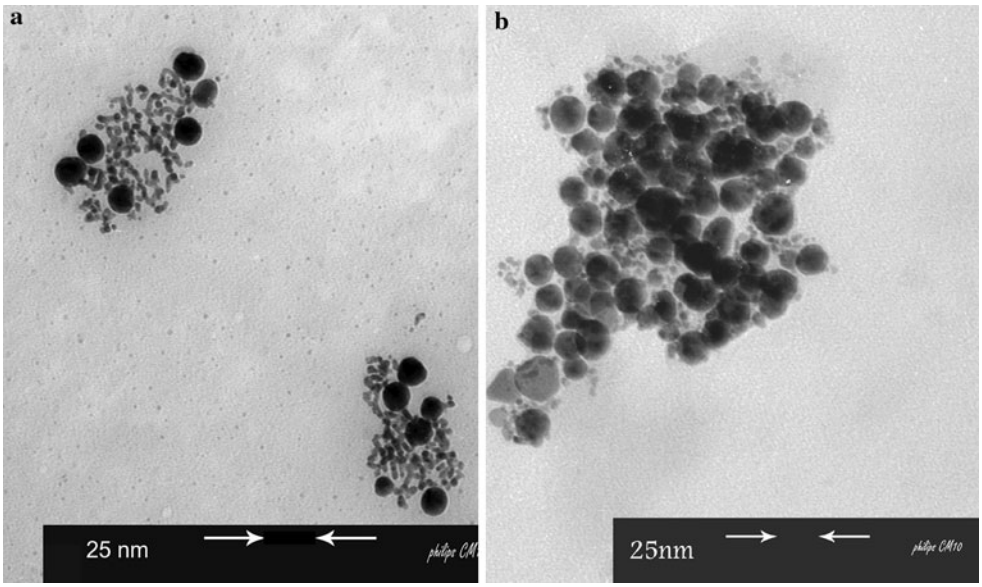
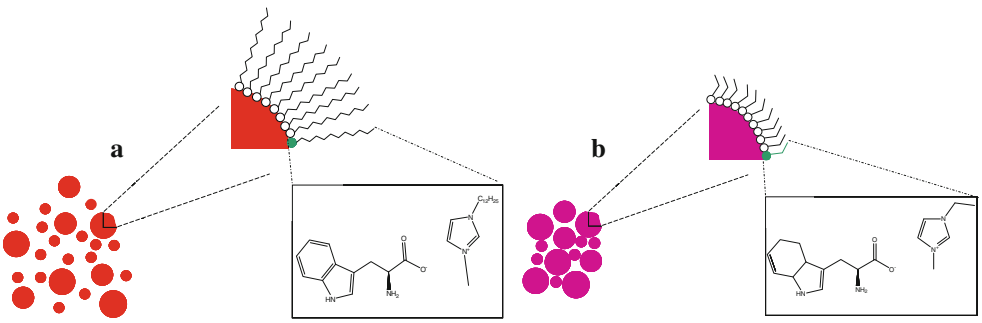


Fig. 3 TEM image of the synthesized gold nanoparticles. **a** AuNP@[C_{12}mim]Trp and **b** AuNP@[C_2mim]Trp



Scheme 3 Schematic structure of the synthesized AuNPs: **a** AuNP@[C_{12}mim]Trp and **b** AuNP@[C_2mim]Trp

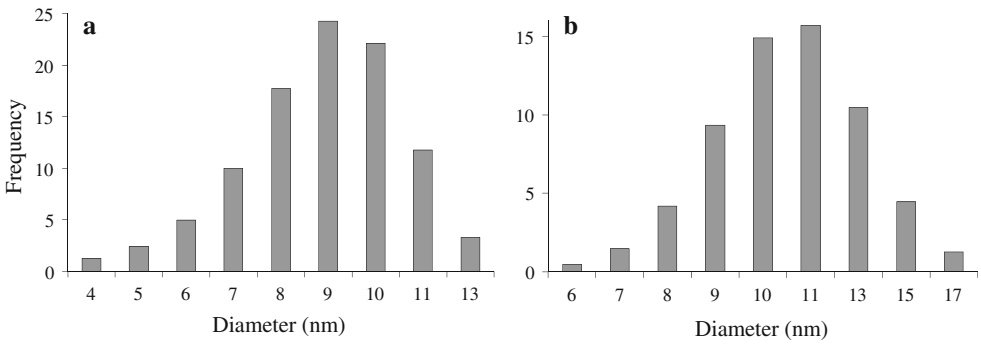


Fig. 4 DLS data of size distribution of **a** AuNP@[C_{12}mim]Trp and **b** AuNP@[C_2mim]Trp

In view of that, the effects of time, of ionic strength of the medium, and the presence of a biological medium were studied.

Effect of time

Figure 5 shows the spectral changes of AuNP@[C_{12}-mim]Trp and AuNP@[C_2mim]Trp after four months. The extent of SPR variations (shift in maximum absorption wavelength, spectral broadening and intensity) shows the amount of stability of AuNPs with time. Low variations of SPR bands along with no precipitation in the solutions reveal that the synthesized AuNPs have a good stability.

Effect of ionic strength

To test the effect of ionic strength of the medium on the stability and dispersibility of the synthesized AuNPs, the

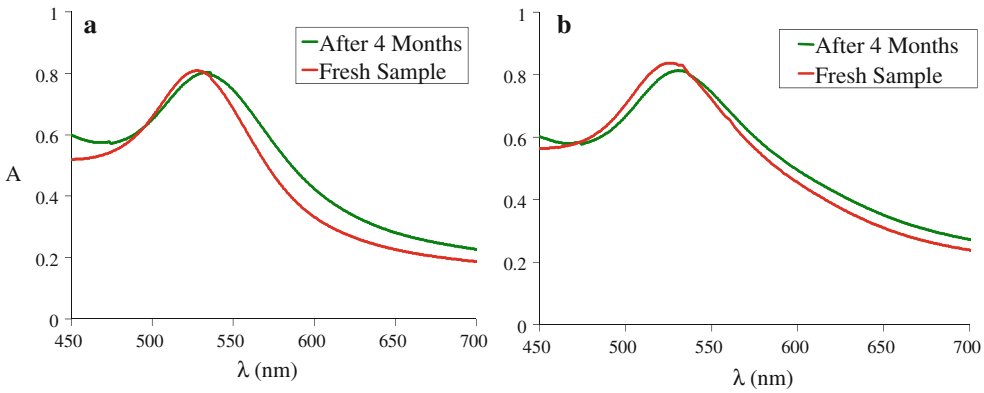


Fig. 5 Spectral changes of **a** AuNP@[C_{12}mim]Trp and **b** AuNP@[C_2mim]Trp

changes in their SPR band were monitored in NaBr solution (Murawala et al. 2009). The spectral changes of AuNPs upon successive injections of 5 μL of NaBr (5 M) solution to 2 ml of AuNPs are shown in the online resource. It can be seen that while AuNP@[C_{12}mim]Br is highly stable in this media, AuNP@[C_{12}mim]Trp and AuNP@[C_2mim]Trp show SPR shifts along with spectral broadening. The amounts and the pattern of SPR shifts are shown in Fig. 6. From the slopes of the graphs, it can be deduced that the stability of AuNP@[C_{12}mim]Trp is higher than AuNP@[C_2mim]Trp in an electrolyte medium.

Effect of biological media

The behavior of the as-prepared AuNPs was also investigated in the presence of a biological medium. To do so, the changes in their SPR band were monitored in Roswell Park Memorial Institute medium (RPMI) which is a biological medium used in cell and tissue culture. It contains different amino acids, vitamins, inorganic salts and other components useful for cell growth. Online resource shows the spectral changes of AuNPs upon successive injections of 5 μL of RPMI to 2 ml of AuNPs.

Contrary to the results of electrolyte medium, AuNP@[C_{12}mim]Br in RMPI has the least stability compared to AuNP@[C_{12}mim]Trp and AuNP@[C_2mim]Trp. The pattern of SPR shifts is shown in Fig. 7. Again from the slopes of the graphs, it can be deduced that the stability of AuNP@[C_{12}mim]Trp is higher than AuNP@[C_2mim]Trp.

From the above data, it can be concluded that the Trp moiety, which is a biomolecule, induces a distinct stabilization to NPs in the biological media due to its resemblance to the surrounding medium. Therefore, it is preferable to use biomolecules as the capping agents of NPs, when it is aimed to use them for a biological purpose.

Another point that should be mentioned is a comparison between the stability of AuNPs capped by [C_{12}mim]Trp and [C_2mim]Trp. From the slopes of the corresponding curves in Fig. 6 and Fig. 7, it is seen that the shifts of SPR band for AuNP@[C_{12}mim]Trp are poorer compared to that of AuNP@[C_2mim]Trp. It can be concluded that [C_{12}mim]Trp exerts a higher amount of stability for AuNPs compared to [C_2mim]Trp.

Conclusion

A novel double-step procedure has been employed for the synthesis of biologically stable hydrophobic AuNPs using AAILs as the capping agent. To the best of our knowledge,

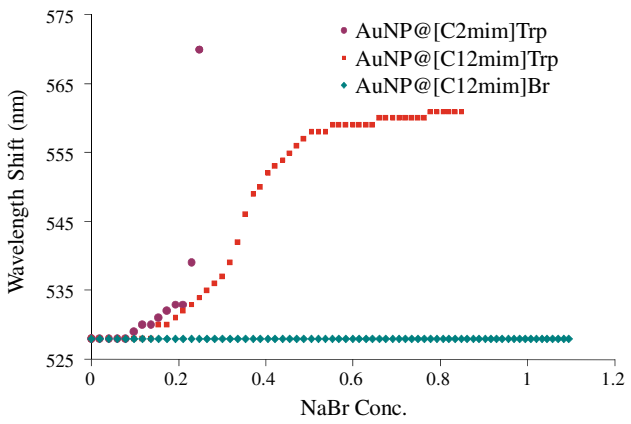


Fig. 6 Pattern of SPR shifts upon injections of NaBr

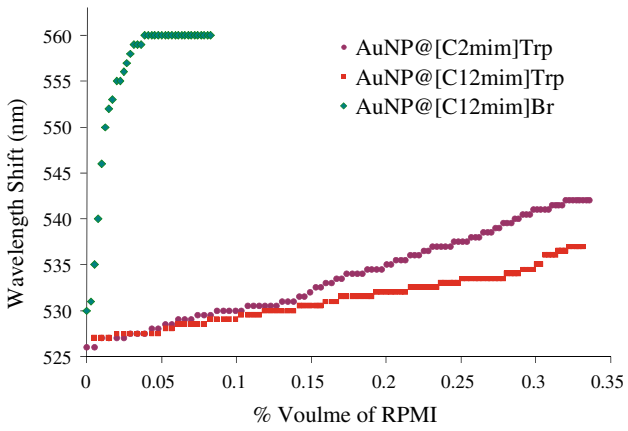


Fig. 7 Pattern of SPR shifts upon injections of RPMI

this is the first report on using these kinds of ionic liquids in the synthesis of AuNPs. The optimum concentrations for the synthesis of AuNPs have been obtained by monitoring surface plasmon resonance and the red color of AuNPs. The results show that higher stability and dispersibility have been achieved using ionic liquids with longer alkyl chain. Moreover, the as-prepared AuNPs demonstrate high stability in biological media which makes them potential candidates for biological purposes.

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Conflict of interest The authors declare that they have no conflict of interest.

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