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Research paper

Synthesis of colloidal Ag nanoparticles with citrate based ionic liquids as reducing and capping agents

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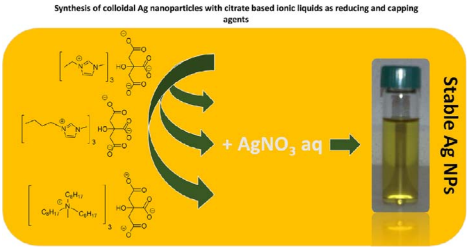
GRAPHICAL ABSTRACT

Synthesis of colloidal Ag nanoparticles with citrate based ionic liquids as reducing and capping agents



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ABSTRACT

The aim of this paper was to synthesize ionic liquids (ILs) that can play the double role of capping and reducing agents for the fabrication of silver nanoparticles (Ag NPs). A new simple method of synthesis of some ILs that have as counter ion citrate and their application in silver and gold nanoparticles preparation will be presented. AgNPs with a medium diameter of 8 nm, stable for more than 7 months in aqueous solution at room temperature were obtained with trioctyl ammonium citrate (TOM_3Citr) at 1:7 molar ratio ($AgNO_3$:TOM_3Citr). The stability of these nanoparticles was investigated with UV–vis spectroscopy and the shape and diameter by TEM characterization. The effect of synthesis conditions was also investigated (molar ratio, temperature, pH) as well as the possibility to use the same IL to prepare Au NPs.

1. Introduction

In the last decades, metal nanoparticles (MNPs) with very small diameters and narrow size distribution have received a great deal of attention from both scientific and industrial researchers. In particular, Ag and Au nanostructures have been considered interesting materials because they have unique optical, electronical, thermal and catalytic properties but also biochemical properties.

Almost in the same time with the development of metal nanoparticles chemistry, ionic liquids (ILs, organic salts liquid at/or near room temperature) captivated the attention of researchers from academia and industry due to their unique physico-chemical properties being proposed as alternative media or components in very wide areas of applications. In the specific field of inorganic materials, they have found increasing application being able to act as solvents, additives, template agents etc., so giving rise to materials with novel morphologies and improved properties to use in catalysis and electrochemistry, to mention just two examples [1,2].

Imidazolium based ILs have been generally used in the synthesis of metal nanoparticles as stabilizing agents. The association of asymmetric organic cations to weakly coordinated anions, such as hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), bis(trifluoromethylsulfonyl)

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imide (Tf_2N^-), gives ionic liquids that possess special properties like high thermal and chemical stability, large electrochemical window, high ion density, low viscosity and negligible vapor pressure [3]. Furthermore, their peculiarity to give self-organization and segregation at the nanomolecular scale, due to the ionic character of the fluids and the presence of non-polar moieties associated with ions [4,5] has been considered a unique positive feature for application in this field. Antonietti et al. in 2004 defines ionic liquids as “an entropic driver”, able to affect the spontaneous ordering of the metal nanostructures [6].

Although the synthesis of metal nanoparticles [7,8] with ILs is no longer a novelty [9–13], there are only a few papers [3,14,15] reporting one pot preparation of silver nanoparticles using IL as both capping and reducing agent. On the other hand, Ag NPs are attractive from more points of view: a) they have a vast area of application from pharmaceutical to nanotechnological areas, and b) a low cost as materials precursors, at least in comparison with Au or Pt. All these applications require however the ability to prepare Ag NPs having appropriate size and shape being these features able to determine the physical properties of the resulting materials.

The design of ILs that can play the double role of capping and reducing agents for the fabrication of silver nanoparticles has been therefore the first target of this investigation. We obtained high quality Ag NPs by a one-step synthesis. We demonstrate the direct preparation of Ag NPs simply using ILs with imidazolium or ammonium cations and citrate as anion and the role of $AgNO_3$ to IL mole ratio over the stability of the resulting colloidal solutions. Moreover, some data about the possibility to use these ILs to prepare Au NPs will be also reported and discussed.

2. Experimental

2.1. Materials

Methanolic solutions of 1-ethyl-3-methyl imidazolium methyl carbonate ([EMIM][$MeCO_3$]), 1-buthyl 3-methyl imidazolium methyl carbonate ([BMIM][$MeCO_3$]), trioctyl methyl ammonium carbonate ([TOM][$MeCO_3$]), were purchased from Proionic. They were used as starting materials for the synthesis of the citrate based ionic liquids. Citric acid was purchased from Sigma Aldrich and the precursor of Ag NPs, $AgNO_3$ was from Riedel de Haen.

2.2. Synthesis of citrate based ionic liquids

To a methanolic solution of [EMIM][$MeCO_3$], [BMIM][$MeCO_3$] or [TOM][$MeCO_3$] an equimolar quantity of citric acid was added. Briefly, 0.03 mol of methanolic solution containing 30% [EMIM][$MeCO_3$], 35% [BMIM][$MeCO_3$] and 43% [TOM][$MeCO_3$] and 0.01 mol of citric acid was mixed under magnetic stirred at room temperature until no CO_2 bubbles were detected (Scheme 1). The product was dried by rotary evaporation and the viscous liquid, obtained in all cases, was analyzed by NMR and IR (Supplementary information Fig. S2).

$EMIM_3$Citrate (IL1). ^{1}H NMR (D2O): δ= 8.63 (s, 3H), 7.39 (s, 3H), 7.33 (s, 3H), 4.13 (q, J = 14,9 Hz, 6H), 3.79 (s, 9H), 2.55 (d, J = 14,9 Hz, 2H), 2.45 (d, J = 14,9 Hz, 2H), 1.40 (t, J = 7,4 Hz, 9H).^{13}C NMR (D_2O): δ = 181.7; 178.5; 135.0; 122.9; 121.3; 74.6; 44.9; 44.2; 35.0; 13.9.

$BMIM_3$Citrate (IL2). ^{1}H NMR (D_2O): δ= 8.64 (s, 3H), 7.39 (s, 3H), 7.34 (s, 3H), 4.10 (t, J = 7,1 Hz, 6H), 3.80 (s, 9H), 2.55 (d, J = 14,9 Hz, 2H), 2.46 (d, J = 14,9 Hz, 2H), 1.75 (m, 6H), 1.22 (m, 6H), 0.83 (t, J = 7,3 Hz, 9H).^{13}C NMR (D_2O): δ = 181.2; 178.4; 135.3; 123.1;121.7; 74.5; 48.7; 44.9; 35.1; 30.8; 18.2; 12.1.

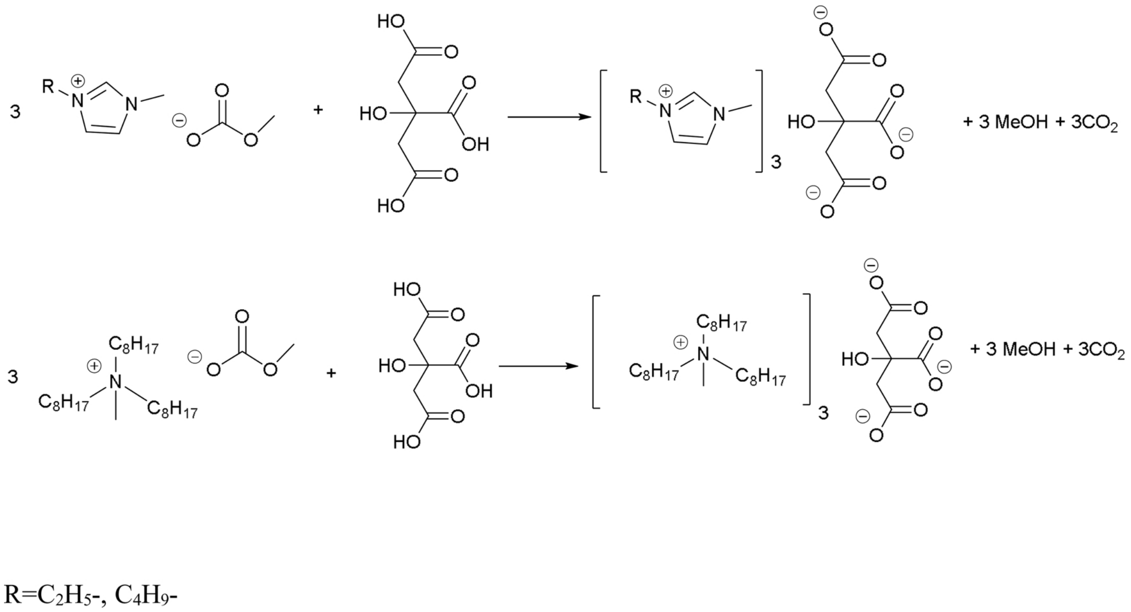
TOM_3Citrate (IL3). 1H NMR (CD_3OD): δ = 3.40 (m, 18H), 3.13 (s, 9H), 2.98 (d, J = 15,1 Hz, 2H), 2.85 (d, J = 15,1 Hz, 2H), 1.81 (m, 18H), 1.45 (m, 90H),1.02 (m, 27H). ^{13}C NMR ($CDCl_3$): δ = 176.38; 60.84; 48.75; 46.00; 31.22; 28.68; 28.58; 25.85; 22.14; 21.85; 13.62.

2.3. Synthesis of Ag NPs

The Ag NPs were synthesized as follows: An aqueous stock solution of $AgNO_3$ (1 mM, 6 mL) was added to a solution (20 mL) of the IL1 or IL2 (concentrations ranging from 0.3 mM to 7 mM) in the same solvent under continuous magnetic stir at the reflux temperature (100 °C). After 70 min, the solution changes from colorless to yellow. UV–vis analysis was performed on collected samples. Samples were stored in the dark at room temperature and at 0 °C and subsequently re-analyzed by UV–vis (1–2 months).

The same procedure was used also for IL3. In this case, due to the low solubility of this IL in water, ethanolic solutions of IL and $AgNO_3$ were employed.

The reactions at pH 3 and 10 were carried out by adding either



Scheme 1. Synthesis of citrate based ionic liquids.