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Regular Article

In situ template synthesis of gold nanoparticles using a bis-imidazolium amphiphile-based hydrogel

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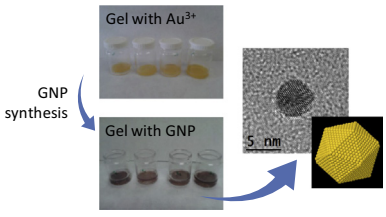
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Gemini-type bis-imidazolium amphiphiles are able to stabilize gold nanoparticles (GNPs) and also form hydrogels. It should be possible to obtain GNPs synthesized within these hydrogels and stabilized by the bis-imidazolium molecules.
Experiments: Hydrogels containing a gold salt were formed using 1,3-bis[(3-octadecyl-1-imidazolio)methyl]benzene dibromide. After aging of the gel, upon addition of the reducing agent in a solvent the formation of GNPs was assessed. The gel was characterised and the GNPs were observed using High Resolution Transmission Electron Microscopy (HRTEM).
Findings: Monodisperse GNPs with an average size of ca. 5 nm and well defined icosahedral geometry were formed *in situ* using the bis-imidazolium amphiphile-based hydrogel as template. Furthermore the gelator is also the stabilizing ligand of the GNPs, allowing the recovery of the GNP by disassembling the gel without aggregation of the inorganic colloid.

1. Introduction

Nanoparticles (NPs) are the focus of increasing attention as drug delivery systems (DDS) with intense research being carried out in the last decade [1,2]. The most commonly used ways to obtain gold nanoparticles (GNPs) are the Brust–Schiffrin method [3], in a biphasic system where a thiol stabilizes the GNPs, and the Turkevich method [4], in aqueous solution where the GNPs are stabilized by the citrate anion through electrostatic interactions. However, alternative ligands used to stabilize GNPs are also viable, such as amines [5], phosphines [6], triazole ring-containing polymers [7], and other polymers that may be synthetic [8] or extracts from natural sources [9,10]. Also, amphiphiles that both reduce and cap the GNPs have been employed [11,12] as well as imidazolium-based amphiphiles [13].

Apart from the syntheses in solution, there have also been methods developed to obtain NPs of gold and other metals using

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gels as templates and adding a reducing agent, normally $NaBH_4$. For example, cobalt [14] and silver NPs have been prepared in hydrogels of pluronic [15], chitosan [16], or poly(acrylamide)/poly(ethylene glycol) [17], to name a few. Poly(ethylene oxide propylphosphonamidate) hydrogels were reported as being able to reduce anions of some metals, obtaining the respective NPs. The metals used were gold, silver, palladium, platinum and ruthenium [18]. Amphiphilic amino acid-based gelators [19,20] and oligopeptide gelators [21] have the ability to reduce the gold ions, allowing the formation of GNPs. Some gels from amphiphilic compounds based on urea [22] and on ascorbic acid [23] have also proved to be able to reduce the gold ions *in situ* and stabilize the resulting GNPs. Furthermore, gels formed by imidazolium-derived ionic liquids have been employed for the synthesis of GNPs by irradiation with UV light [24]. The gels acts as template matrix, to control the size of the NPs, but also prevents their aggregation. The NPs included in the gel can form a composite with a defined function, for example as catalyst [18], sensor [25] or antibacterial material [15].

In this paper we sought to develop an alternative medium for the formation of GNPs that could provide synthetic and structural versatility. We have found that this simple method can produce very well defined colloids, with improved size distribution. Furthermore, the bis-imidazolium gelator used is an ionophore [26,27] meaning that, compared with other examples in the literature, the synthesized GNPs can incorporate anions without further modification. We describe the formation of GNPs using a recently reported hydrogel [28] of 1,3-bis[(3-octadecyl-1-imidazolio) methyl]benzene dibromide (**1·2Br**) (Fig. 1) as a matrix. The gel used as the template medium was formed by adding an aqueous solution of $HAuCl_4$ to an ethanolic solution of the gelator **1·2Br**. The gel was characterised by Atomic Force Microscopy (AFM), Cryo-Transmission Electron Microscopy (Cryo-TEM) and the rheological behaviour was studied. The synthesized GNPs were characterised by UV–visible absorption spectroscopy, X-ray Photoelectron Spectroscopy (XPS) and High Resolution Transmission Electronic Microscopy (HRTEM).

2. Experimental section

All reagents were of analytical grade. The compound 1,3-bis[(3-octadecyl-1-imidazolio)methyl]benzene dibromide (**1·2Br**) was prepared as reported previously [13].

2.1. Preparation of gels and synthesis in situ of GNP

The gels were prepared as follows: gels A1 and B1 (with a molar ratio **1·2Br**:Au of 10:1) were prepared with 10 mg of **1·2Br** dissolved in 0.8 mL of ethanol and 0.7 mL of ethanol (respectively). Then, 216 μL of a 2 mg mL^{-1} aqueous solution of $HAuCl_4{\cdot}3H_2O$ was added and the volume was completed with MilliQ water until a final volume of 2 mL. Gels A2 and B2 (with a molar ratio **1·2Br**:Au of 8:1) were prepared with 10 mg of **1·2Br** dissolved in 0.8 mL of ethanol and 0.7 mL of ethanol (respectively). Then, 270 μL of a 2 mg mL^{-1} aqueous solution of $HAuCl_4{\cdot}3H_2O$ was added and the volume was completed with MilliQ water until a final volume of 2 mL.

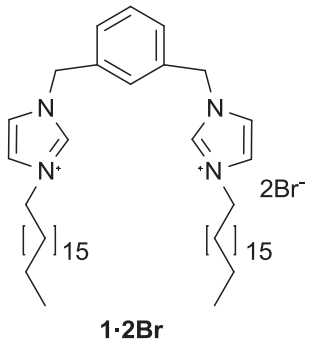

Fig. 1. Structure of the gelator molecule **1·2Br.**

The gels were left overnight for proper aging, because the gelling process occurred slowly. To prepare the GNP, 12 equivalents (with respect to Au^{3+}) of an aqueous solution of $NaBH_4$ were added to the gels, in a final volume of 2.5 mL. The solution was left in contact with the gels for 8 h, then it was removed and the gels were washed with water using a micropipette.

2.2. Characterisation methods

AFM images were recorded by the Scanning Probe Microscopy Service in the ICMAB-CSIC on a PicoSPM system (Molecular Imaging). The intermittent contact mode was used close to resonance frequencies of the silicon cantilevers (Nanosensors, FM type force constant 1.2–3.5 N/m and tip diameter 5 nm) of around 60–70 kHz. All the images were recorded under atmospheric conditions. Samples were obtained by a cross-section cut of the gel from two different areas (from the centre of the gel and from the edge of the gel) and placing the sample on a freshly cleaved mica surface and were left to dry in air.

Transmission Electron Microscopy using Freeze Fracture Direct Imaging was performed as follows: the GNP-containing gel sample, collected by cross section cutting of the gel, was sandwiched between two copper platelets using a glow-discharged holey carbon grid as spacer. Then, the samples were frozen by liquid ethane immersion, and fractured later into liquid nitrogen. The grid with the fractured sample was transferred to a microscope Tecnai F20 (FEI Company, Eindhoven, Netherlands) using a Gatan cryo-holder (Gatan, Pleasanton, CA). The images were taken at 200 kV with a 4096 × 4096 pixel CCD Eagle camera (FEI Company, Eindhoven, Netherlands) at a temperature between −170 °C and −175 °C and using low-dose imaging conditions.

The rheological study of the flow behaviour was performed with a HAAKE Rheostress1 rheometer (Thermo Fisher Scientific, Karlsruhe, Germany) connected to a Thermo Haake Phoenix II + Haake C25P temperature controller. The rheometer was equipped with a cone-plate geometry set-up with a fixed lower plate and a mobile upper cone (Haake C60, 2° 60 mm diameter, 0.106 mm) and also a plate–plate geometry (PP60 Ti, 60 mm diameter, 0.5 mm gap between plates). The study was carried out on a freshly prepared sample obtained in a Petri dish with the same diameter as the plate, so that the sample could be transferred to the rheometer and analysed without any deformation of the gel. The rheometer was connected to a computer provided with the software HAAKE RheoWin®Job Manager V.3.3 to carry out the test and RheoWin®Data Manager V.3.3 (Thermo Electron Corporation, Karlsruhe, Germany) to carry out the analysis of the obtained data. Viscosity curves and flow curves were recorded under rotational runs at 32 °C for 3 min during the ramp-up period from 0 to 100 s^{-1}, 1 min at 100 s^{-1} (constant share rate period) and finally 3 min during the ramp-down period from 100 to 0 s^{-1}.

UV absorption spectra were obtained on UV-1800 Shimadzu UV Spectrophotometer. The GNP sample was suspended in dichloromethane and placed in a quartz cuvette.

XPS experiments were performed at the *Centres Científics i Tecnològics de la Universitat de Barcelona* (CCiTUB), in a PHI 5500 Multitechnique System (from physical electronics) with a monochromatic X-ray source (Aluminium Kalfa line of 1486.6 eV energy and 350 W), placed perpendicular to the analyser axis and calibrated using the 3 $d_{5/2}$ line of Ag with a full width at half