



A tri-block copolymer templated synthesis of gold nanostructures

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ABSTRACT

Stable ultra-small gold nanoparticles have been synthesized in aqueous phase by using a tri-block copolymer (BMB) as a templating agent consisting of two PEG-methylacrylate chains (B blocks) anchored to a poly(methacrylic) moiety containing a trithiocarbonate unit (M block). The effect of the BMB/Au molar ratios on the final particle size, shape and monodispersity has been investigated. The synthesized nanosols have been characterized by means of Visible Absorption, Small Angle X-ray Scattering (SAXS), and Transmission Electron Microscopy (TEM). Results clearly indicate that the polymer plays a key role in determining the size and shape of gold particles, from fractal-like structures to monodisperse spherical particles with a mean diameter of about 3 nm. The aggregation behavior of these nanostructures has been characterized both in solution (SAXS) as well as on mica substrate (AFM) and has been proven to be driven by the polymer to gold concentration ratio.

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1. Introduction

The synthesis of gold colloids is one the major topics in material science since the discovery of nanoparticles in 1867 by Michael Faraday. Thanks to their optical properties, these materials have a wide range of applications in different fields, ranging from biology to chemistry and nanotechnologies: i.e., molecular recognition [1–3], enhanced bio-sensing [4–6], and catalysis [7]. These properties are strictly size dependent and for this reason the preparation method has to be properly chosen to produce particles with desired characteristics. The synthesis and characterization of gold or gold alloys particles from about 1 nm to several micrometers has been recently reported [8–15].

The phase transfer method, originally developed by Brust et al. [16], uses a reducing agent (usually NaBH₄) dissolved in the aqueous phase, and a thiolated capping agent in the organic phase. The gold nuclei are produced and grown in the water phase, then are chemically coated by thiolated hydrophobic molecules and transferred to the oil phase [17–20]. This method has high reaction yields and produces nearly monodisperse particles. Moreover it allows a significant flexibility in choosing the particle size by controlling the reaction conditions. Two limitations are associated to the use of phase transfer method: an organic phase is necessary

and the nanoparticle surface gets covalently coated. As a matter of fact, once the thiolated molecules are chemically bound to the nanoparticle surface, it becomes difficult to modify the surface of the particle to introduce new functionalities for specific applications.

The most classical method to produce gold hydrosols is the citrate reduction in water solution (*Turkevich method*) [21]. Numerous variations of this procedure are reported in literature, where the citrate has been substituted with ascorbic acid [22], polyacrylic acid [23] and other reagents. This synthetic approach has the advantage of being entirely carried on in the water phase, without the necessity of transferring the nanoparticles in a second phase once they are prepared. On the other hand, the amount of produced particles is quite low. Moreover, the particle size range that can be obtained by this approach is not very large. Seeding growth methods have been developed to overcome this limitation [24–26]. In this approach small metal particles are prepared first and later used as seeds (nucleation centres) for the growth of larger particles with controlled dimension.

The need to prepare nearly monodisperse gold nanoparticles with a functionalizable surface took to the design of new hydrophilic capping agents [27–31]. In particular, Hussain et al. [27] reported on the possibility of obtaining monodisperse gold nanoparticles in the 1–4 nm size range in water in the presence a water-soluble alkyl thioether end-functionalized poly(methacrylic acid) stabilizer. The authors emphasized that the ratio of gold to capping ligand precisely controls the particle size. Later, Wang

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et al. [28] investigated in details the effect of the concentration, structure, and “denticity” of the stabilizing polymer on the particle size distribution. Recently, Du et al. [32] described the synthesis of gold nanoparticles (AuNPs) in *N,N*-dimethylformamide (DMF) by using amphiphilic multiblock copolymers as templating agents, obtained by polymerization of styrene (S) and 4-vinylpyridine (4VP) with cyclic trithiocarbonate as RAFT (Reversible Addition–Fragmentation chain Transfer) agent. They produced stable gold nanoparticles directly in DMF. The sizes of the AuNPs slightly increased with raising the concentration of gold salt for a given concentration of the stabilizing agent. The amphiphilic character of the multiblock copolymers enabled the transfer of AuNPs from DMF into an aqueous medium.

In this paper we report the direct synthesis of ultra-small gold nanoparticles in water phase with NaBH_4 as reducing agent and in the presence of a tri-block copolymer as capping agent. The BMB polymer consists of two PEG-methylacrylate chains (B blocks) anchored to a poly(methacrylic) moiety containing a trithiocarbonate unit (M block). Since the gold/BMB molar ratio is a critical parameter in controlling the particle size [27,33], different ratios have been explored to investigate their effect on the morphology and to optimize the experimental conditions.

2. Material and methods

$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was purchased from Sigma–Aldrich; NaBH_4 and the monomers used for the synthesis were purchased from Aldrich Chemicals (Milan, Italy). Methacrylic acid (MAA) was distilled at reduced pressure and only the fraction boiling at 65 °C was used. Oligo(ethylene glycol) methylether methacrylate $M_n = 475$ Da (OEGMA, $d = 1.08$ g/mL at 25 °C) and the initiator 4,4'-azobis(4-cyanopentanoic acid) (V-501) were purchased from Aldrich and used without further purifications.

The RAFT chain transfer agent (CTA) *S,S'*-bis(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate was synthesized according to the procedure reported by Lai et al. [34]. All the solvents were reagent grade and were used without further purification; HPLC-grade water was used for the polymerization while for the synthesis of the nanoparticles water purified with a Millipore system has been employed (resistivity >18 M Ω cm).

2.1. Copolymer synthesis

The RAFT synthesis of the poly(OEGMA-*b*-MAA-*b*-OEGMA) BMB-type, consisting of methacrylic acid (M block) and oligo(ethylene glycol) methylether methacrylate (B block), was carried out by polymerizing sequentially the two monomers, starting with OEGMA, and using *S,S'*-bis(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate as the RAFT agent of the controlled free radical process.

A round-bottomed flask was loaded with water (100 mL), OEGMA (8 g, 1.68×10^{-3} mol), CTA (0.45, 1.6×10^{-3} mol) and purged 30 min with N_2 . The reaction mixture was heated to 70 °C with a thermostated oil bath, under nitrogen atmosphere and magnetic stirring, and the V-501 (15 mg, 5.3×10^{-5} mol) initiator was added to start the polymerization. The reaction was interrupted after 3 h by cooling down the reactor to room temperature.

The polyOEGMA homopolymer and RAFT macro-transfer agent for the subsequent block copolymerization were purified from unreacted monomer by dialysis against water (membrane cut-off = 2 kDa). After the purification the residual content of OEGMA monomer was below 2% as determined by ^1H NMR.

Size exclusion chromatography (SEC) analysis was performed using two Ultrahydrogel Linear columns with a guard precolumn and an aqueous buffer (NaHCO_3 0.05 M, NaNO_3 0.1 M, triethanolamine 0.02 M, NaN_3 0.03%) as eluent to determine molecular weight

and polydispersity index I_d . A set of poly(ethylene oxide) standards (400; 1000; 4000; 8000; 12,000; 20,000; 40,000 Da) was used for column calibration. The calculated and experimental values for the synthesized blocks are reported in Table 1.

The second step of the synthesis of the block copolymer is analogous to the first one. In this case the polyOEGMA macro-transfer agent (8 g) is used instead of the CTA to polymerize methacrylic acid (10 g, 0.12 mol) together V-501 (15 mg, 5.3×10^{-5} mol) initiator.

The synthesized BMB copolymer was lyophilized and purified by extraction in soxhlet for 12 h with CHCl_3 . After this procedure only some traces of residual acid monomer could be detected by ^1H NMR.

In Table 1 the values of the molecular weights and polydispersity index, as determined by SEC, of the copolymer are reported. The copolymer structure is shown in Fig. 1.

2.2. Nanoparticle synthesis

Gold nanoparticles were synthesized in water solution in the presence of the BMB polymer. Three different BMB amount were added to a 3×10^{-4} M solution of the gold precursor ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), in order to evaluate the influence of the polymer concentration on the final shape and size of the nanostructures: in particular gold/BMB molar ratios of 1000, 215 and 4.6 were used, herein after referred as sample A, B and C respectively. The reduction was performed at 0 °C by adding the proper amount of ice-cooled 0.1 M NaBH_4 . The reducing agent addition has been performed at a rate of 100 $\mu\text{L}/\text{min}$. Final concentration of about 0.2 mg gold/mL was obtained for all the gold dispersions. The samples containing the capping polymer remain stable for several months, while in a “blank” sample, where the gold salt reduction was performed without BMB polymer, precipitation occurred within a few hours.¹ This different behavior highlights the role of the polymer chains in enhancing the nanosols stability. The synthesis has been performed at pH 5.5 units because recent studies [35] revealed that the polymer has the best conformation for our purposes at this pH. At pH values higher than 5.5, the methacrylic moieties undergo to a full deprotonation and change to a more hydrophilic character; the ultimate consequence is the formation of a unimolecular micellar structure with the ionized block pulled towards the solvent and the PEG chains arranged to form the micellar core. At pH equal or lower than 5.5, the PEG and methacrylic moieties are both available to template and stabilize the gold nanosol.

2.3. Physico-chemical characterization

2.3.1. Small Angle X-ray Scattering

SAXS measurements were carried out with a HECUS SWAX-camera (Kratky) equipped with a position-sensitive detector (OED 50 M) containing 1024 channels of width 54 μm . Cu K α radiation of wavelength 1.542 Å was provided by a Seifert ID-3003 X-ray generator (sealed-tube type), operating at a maximum power of 2 kW. A 10 μm thick nickel filter was used to remove the Cu K α radiation. The sample-to-detector distance was 275 mm. The scattering path between the sample and the detector was kept under vacuum ($P < 1$ mbar) during the measurements to minimize scattering from the air. The Kratky camera was calibrated using silver behenate, which is known to have a well-defined lamellar structure ($d = 58.38$ Å) [36]. Scattering curves were monitored in a Q -range from 0.009 to 0.55 \AA^{-1} . Q , the scattering vector, is defined

¹ Blank sample has been prepared reducing gold precursor in water without polymer using the same experimental conditions (gold concentration, reduction method). This reduction leads to an unstable sample, and precipitation of the reduced products occurred within few hours, while samples A, B and C are stable for months.

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