Green photocatalytic synthesis of stable Au and Ag nanoparticles

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Stable Au and Ag nanoparticles with diameter 5–10 nanometers were synthesized in water at pH 7 and at room temperature by a novel green photocatalytic method. The method features very low energy consumption and non-toxic reagents with high yields of concentrated nanoparticles in aqueous solution obtained in less than four minutes. The nanoparticles so obtained are highly monodispersed, thus avoiding the use of further time consuming and cumbersome purification procedures. In addition, the capping agent is readily exchanged by thiols, providing a facile way of functionalization for biological applications.

Introduction

Nanoparticle (NP) synthesis using a green chemistry route is a promising avenue of research in nanoscience today.[1,2] Several synthetic methods relying on green chemistry have so far been described, especially for noble metal nanostructures including nanospheres,[3-5] nanorods and nanowires.[6-8] Green chemistry synthetic approaches must be designed for reduced environmental impact; waste reduction; process safety; materials, and energy efficiency. Especially favored are methods that do not rely in large amounts of solvent for NP purification and size selection implying a one-step synthesis of mono-dispersed products.[2] Efficient synthetic pathways that can be carried out at ambient temperature are preferred over methods of NP synthesis conducted at elevated temperatures.[1] This is seldom the case for water-based synthetic methods. For instance, the widespread citrate-based method proposed by Turkevich relies on high temperature;[6] and strong reducing agents like sodium borohydride are used for room temperature synthesis.[7]

Most of the synthesized gold and silver NPs are nowadays finding uses in biological applications from novel biosensing devices[9,10] to cancer therapy;[11] being thus mandatory that the synthesized NPs are water-soluble and easily functionalized for surface chemistry fine-tuning. The development of bulk solution synthetic methods in water that can save energy and reagents while allowing high yields of NPs with low size dispersion is of paramount importance for the full implementation of a green chemistry synthetic strategy in NPs intended for biological applications.

Several photochemical methods for the synthesis of metal NPs have been reported, either by direct photoreduction of a metal precursor, or with photosensitizers as intermediate species. Photochemical methods have several advantages for the synthesis of NPs, namely high spatial resolution, controllable *in situ* generation of reducing agents, and versatility.[12] The present method combines the advantages of a photochemical method, with those of using a catalysis reaction. Catalysis has been recognized as one of the main tools for implementing green chemistry procedures, allowing improved yields, increased selectivity, use of catalytic *versus* stoichiometric amounts of materials, and lower energy requirements.[1]

A tin(IV)-porphyrin complex (SnP) has been previously used as a photocatalyst in the synthesis of platinum NPs.[13] In the photocatalytic cycle, a reduced SnP$^{-\bullet}$ is formed, and this highly reducing agent readily transfers one electron to the precursor metal cation, regenerating the SnP species and initiating the formation of NPs. The metal atoms thus formed in solution assemble to form "seed" nuclei, that continue to grow either by direct reduction of the metal cation at the NP surface or by aggregation and fusion. The use of the photocatalyst allows controlling the rate of seeding/growth either by changing the concentration of the photocatalyst or light intensity, and thus represents a convenient way to kinetically control the final NP size and size dispersion.

Herein, we describe a method that relies on a photocatalytic reaction to produce gold and silver NPs with enhanced monodispersion in an aqueous medium, at pH 7 and room temperature. A tin(IV)-porphyrin complex is used as photocatalyst, that allows fast formation of seeds in solution, leading to superior size-dispersion of the final NPs. This one-pot seeding method engages the following green chemistry principles: (*i*) low energy consumption, the reaction is carried out at room temperature and uses a low-power halogen bulb for photocatalysis; (*ii*) short reaction time, the complete synthesis takes less than 4 minutes; (*iii*) non-toxic reagents, triethanolamine (TEA) is the electron donor and toxic surfactants that are generally used as capping agents are replaced by poly(N-vinyl pyrrolidone) (PVP), a water soluble polymer that is physiologically compatible; (*iv*) no

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purification is necessary; a mono-dispersed NPs solution is readily obtained. Furthermore, the NPs can be easily functionalized with a thiolated ligand, imparting new functionalities to the NPs that can be explored for biological applications.

Results and discussion

The photocatalytic method

The photocatalytic method as described in Scheme 1 was used to synthesize Au and Ag NPs. Variations of this method have been successfully utilized before to grow Pt nanostructures on surfactant templates[13–15] or on peptide-nanotubes.[16] The photocatalyst used here was a tin(IV)-porphyrin complex, Sn(IV) tetra(N-methyl-4-pyridyl) porphyrin tetratosylate chloride (SnP). The photocatalytic reduction of gold and silver salts is accomplished in the presence of visible light and an electron donor (TEA). Absorption of light by SnP in the presence of the electron donor yields the long-lived radical ion, $SnP^{-\bullet}$, a strong reductant ($SnP/SnP^{-\bullet}$, reduction potential of -0.66 V)[13] capable of effectively reducing Au^{3+} to Au° (reduction potential of 1.50 V), and Ag^+ to Ag° (reduction potential of 0.80 V).
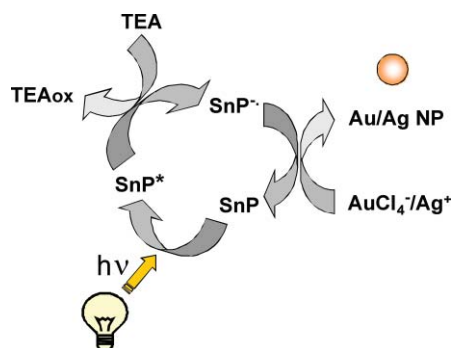
Scheme 1 Reactions involved in the photocatalytic synthesis in aqueous solution, pH = 7, at room temperature. PVP was used as capping agent at an ideal molar ratio of [PVP(monomer)]/[HAuCl₄] = 67.5 for AuNP and [PVP(monomer)]/[AgNO₃] = 107 for AgNP. SnP* = porphyrin in an excited triplet state; $SnP^{-\bullet}$ = porphyrin radical anion.

Kinetic control granted by the porphyrin seems to be critical for this photocatalytic method. The influence of irradiation time on the reaction course is presented in Fig. 1 for Au and Ag NPs. UV-visible spectra of nanoparticle growth followed by the intensity increase of the surface plasmon resonance band revealed that the synthesis reaction is finished with maximal nanoparticle formation, after a 4 minutes irradiation period, for both Au and Ag NPs. Stoichiometric reduction and absence of unreduced gold and silver salts was confirmed by adding sodium borohydride to the reaction vials. As no further NP formation was observed, it could be concluded that all the gold and silver salts had already been reduced to NPs by the photocatalytic reaction.

Optimization of the synthetic scheme

Poly(N-vinyl pyrrolidone) (PVP) was the capping agent selected for maximum efficiency in NPs formation. The utilized PVP had 360 monomers per polymer molecule for a polymer average molecular weight of 40 000. Other two groups of capping
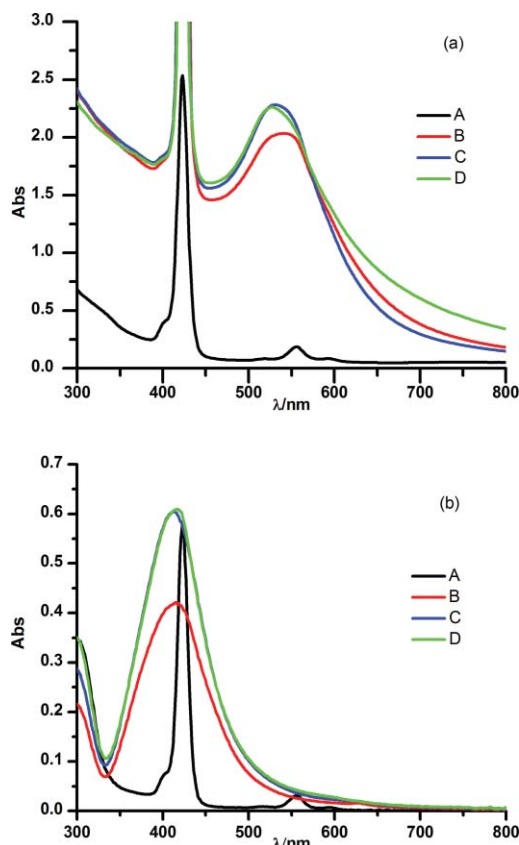

Fig. 1 UV-visible spectra of AuNP (a), and AgNP (b) growth followed by the intensity increase of the surface plasmon resonance band centered at 520 nm (AuNP) and 420 nm (AgNP). Irradiation times were 0 min (A); 2 min (B); 4 min (C); and 10 min (D). Bands observed before irradiation (0 min, trace A) originate from SnP and were subtracted from AgNP spectra to avoid superposition with the plasmon band.

agents were tried, sodium citrate and glycine on one hand and HEPES (4-(2-hydroxyethyl)-1-piperazine-ethanesulfonic acid), cysteine and thiosalicylic acid on the other hand. The first group lead to aggregation and/or larger particles with non-spherical morphology as evaluated by broad plasmon resonance bands in the UV-visible spectra. For the second group of capping agents, all of which contain sulfur in their chemical structure, no formation of NPs could be detected after 1 hour of irradiation.

Optimization of the reaction conditions was pursued in terms of maximal conversion for minimal reaction times and minimal energy spending, in the context of the proposed green chemistry approach.

A molar ratio [PVP]/[HAuCl₄] = 67.5, based on the PVP monomer, was found to be optimal for the formation of spherical AuNPs with low dispersion, as determined by Dynamic Light Scattering (DLS) and Transmission Electronic Microscopy (TEM). Fig. 2 shows a representative micrograph of spherical AuNPs with an average diameter of 8 ± 4 nm. The hydrodynamic diameter as determined by DLS was 17.0 ± 5.0 nm. In the case of silver nanoparticles the optimal molar ratio [PVP]/[AgNO₃] was found to be 107 resulting in the formation of AgNPs with an average diameter of 5 ± 2 nm as determined by TEM (Fig. 3), in good agreement with the hydrodynamic diameter as determined by DLS of 7.3 ± 1.8 nm. The increased diameters
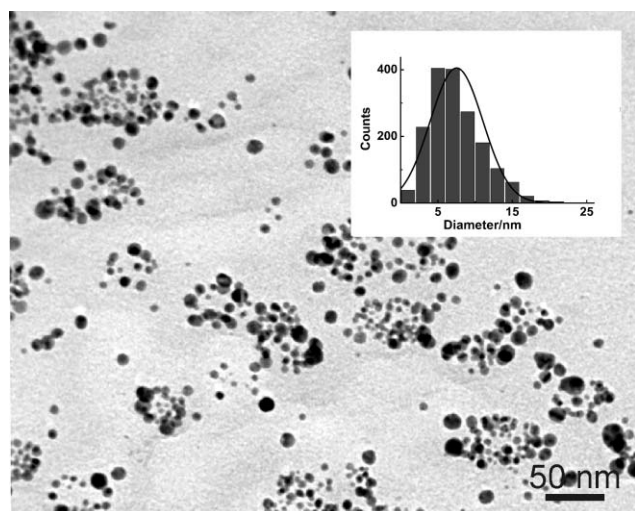
Fig. 2 Representative TEM micrograph of AuNPs synthesized using the photocatalytic method described in Scheme 1. Inset: histogram of NP size distribution with an average diameter of 8 ± 4 nm.
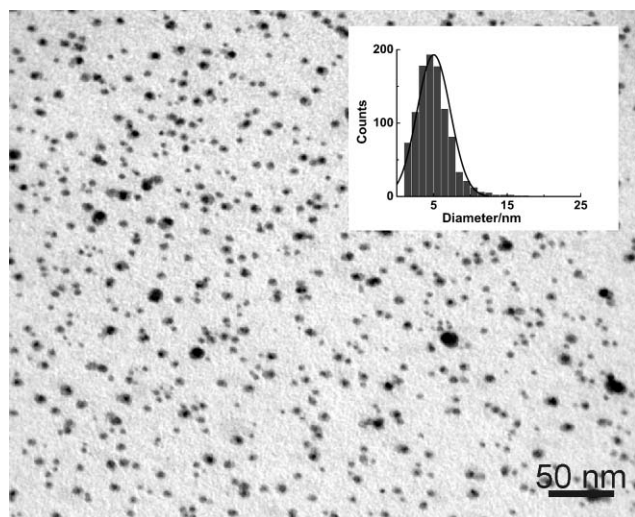

Fig. 3 Representative TEM micrograph of AgNPs synthesized using the photocatalytic method described in Scheme 1. Inset: histogram of NP size distribution with an average diameter of 5 ± 2 nm.

determined by DLS in comparison with TEM determinations, can be explained as DLS measures hydrodynamic diameters of particles, including its hydration sphere. In the present case those diameters probably correspond to a hydrated PVP-based polymer layer. The increase of diameter as measured by DLS in comparison to TEM is *ca.* 1.5 times for AgNPs but is *ca.* 2.1 times in the case of AuNPs. Considering that the molar ratio of PVP that was used for the synthesis of AgNPs is almost double than for the synthesis of AuNPs, these diameter discrepancies suggest that the affinity of the AuNPs for PVP is much higher than that of the AgNPs.

Hoppe *et al.*[17] have synthesized Au and Ag NPs in water, using PVP both as a capping, and a reducing agent *via* radicals generated by the polymer. The authors observed room temperature formation of NPs although the characteristic plasmon

resonance appeared in solution only about 40 minutes after reagent mixing, a timescale that is one order of magnitude higher that our method. Even if this competing reaction is present in our system, no metal salt would be available as the photocatalytic reaction uses all the available metal salt after the initial 4 minutes of reaction, as proven by tentative further reduction with sodium borohydride.

The concentration of the photocatalyst did not seem to influence the size and shape of the NPs obtained, at least for low concentrations (6–12 μM), whereas at higher concentrations (>20 μM), the NPs sizes are highly dispersed and are probably larger, as judged by a broadened plasmon resonance observed by UV-visible spectroscopy. This result is in agreement with the photocatalytic reaction catalyzed by the porphyrin being responsible for the formation of nucleation seeds[13,18] that further grow chemically by direct reduction of Au(III) at the surface of the seeds. For this reason, the present method can be considered a one-pot seeding method in which seeds are formed photocatalytically and NPs grow homogeneously by chemical reduction, generating spherical NPs of controlled size.

Stability of the nanoparticles in solution

The stability of the obtained NP colloidal solutions was evaluated in terms of pH- and salt-induced aggregation. The solutions were stable to pH variations in the range 1.9–10.7 and salt (KBr and KCl) concentrations up to 1 M, showing no signs of aggregation under these experimental conditions. These results agree with previous observations in PVP-stabilized Ag and Au NPs[17] and are a clear evidence of the protecting role of PVP against aggregation. PVP is a neutral polymer, thus not presenting electrostatic interactions with ions in solution, which could lead to NPs aggregation.

Functionalization of the nanoparticles

The obtained NPs in solution could be easily functionalized, as demonstrated by substitution of the PVP capping simply by adding a 11-mercapto-undecanoic acid ethanolic solution to the NP solution. The presence of a carboxylic functionality in the NPs was further demonstrated by the acidification of the medium, which led to a red-shift of the plasmon resonance (Fig. 4). This observation confirms the substitution of PVP by carboxylic moieties that were neutralized by the acidification of the solution, causing the functionalized NPs to aggregate.

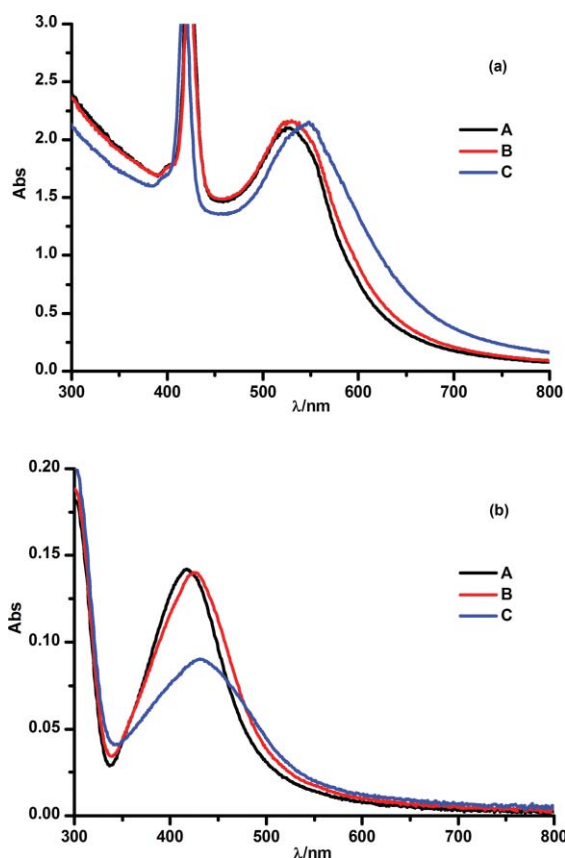### Experimental details

Materials

Fig. 4 UV-visible spectra of Au NPs (a) and Ag NPs (b) before (A) and after functionalization with 11-mercapto-undecanoic acid (B). Upon acidification of the medium, a red-shift of the plasmon resonance occurred (C), due to aggregation of the functionalized NPs, which confirms a successful functionalization.

TEM and DLS experimental procedures

Samples for TEM analysis were prepared by depositing 10 µL of the as-prepared colloidal suspensions in carbon copper grids, washing twice with 10 µL of Milli-Q water, and air dried. TEM was performed with a HITACHI H-8100 microscope operated at 200 kV. Histograms of the NP size distribution (Fig. 2) were generated with ImageJ, a freely available image analysis program (http://rsb.info.nih.gov/ij/); and are based on the counting of 1730 or 1081 NPs, for AuNP or AgNP, respectively.

DLS measurements were made in a Zetasizer Nano ZS from Malvern Instruments. A 4 mWHe-Ne laser (633 nm) was used with a fixed 173° scattering angle. All measurements were carried out at 25 °C. One milliliter of the sample was transferred to a disposable sizing cuvette (Malvern Instruments) and 2 minutes were allowed for the sample to reach thermal equilibrium.

Au and Ag nanoparticles synthesis

In a typical synthesis, reagents were 100 µl of 20 mM HAuCl$_4$; 750 µl of 150 mM triethanolamine (TEA); 1350 µl of 100 mM poly(N-vinyl pyrrolidone) (PVP) K30; 100 µl of 200 µM Sn(IV) tetra(N-methyl-4-pyridyl) porphyrin tetratosylate chloride (SnP) and water to a final reaction volume of 2.5 ml. The final pH of the solution was 7. All the reagents were added to a

4 ml glass vial, and the reaction was started at room temperature by irradiation of the vial with a white light halogen bulb with a power of 50 W. The light bulb was placed at a convenient distance to avoid heating the solution (>20 cm).

After optimization for maximal NPs concentration, reagent concentrations in the reaction vial were as follows: [HAuCl$_4$] = 0.8 mM; [TEA] = 45 mM; [SnP] = 8 µM; [PVP] = 54 mM, for a molar ratio [PVP]/[HAuCl$_4$] = 67.5 (based on the PVP monomer), or in the case of silver NPs: [AgNO$_3$] = 0.56 mM; [TEA] = 40 mM; [SnP] = 16 µM; [PVP] = 60 mM, for a molar ratio [PVP]/[AgNO$_3$] = 107. As reduction is stoichiometric, reduced metal concentrations are 0.8 mM for AuNPs and 0.56 mM for AgNPs.

Conclusions

In conclusion, we have developed an effective, green synthetic method for gold and silver nanoparticles, based on a photocatalytic reaction. The reactions in neutral aqueous solution yield millimolar-range concentrations of reduced gold and silver and are complete within less than 4 minutes at room temperature. The capping agent used for colloidal stabilization of the NPs is easily exchanged allowing further functionalization of the nanoparticles with a thiolated ligand, thus extending the range of applications of these NPs. The obtained nanoparticles are highly monodisperse and further solvent-intensive isolation or purification procedures are not necessary.

The proposed environmentally benign and general approach may find various biological and technological applications, and is currently being tested for other noble metals such as Pt and Pd, and Au–Ag alloys.

Acknowledgements

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