Scalable heterogeneous synthesis of metallic nanoparticles and aggregates with polyvinyl alcohol

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Received 27th October 2008, Accepted 19th December 2008
First published as an Advance Article on the web 12th February 2009
DOI: 10.1039/b819027e

Here we report on a new route to synthesize colloidal silver and gold nanoparticles, potentially scalable for massive nanoparticle-production. This method is based on the microwave-assisted heterogeneous reduction of the metal salts with polyvinylalcohol. The reaction is carried out in alcohols, which are non-solvents for polyvinylalcohol. Nanoparticles can be very easily separated by filtration. The reaction kinetics are extremely fast. Size-controlled formation of nanoparticle agglomerates is accomplished with a seed-mediated synthesis of nanoparticles upon MW exposure.

Introduction

Metal nanoparticles have attracted much attention in recent years because of the effects that quantum -confinement plays on their electronic, magnetic and other related properties. Noble metal nanoparticles such as Ag, Au and Cu possess a very strong absorption in the near UV and visible spectrum. These amazing optical properties arise from an electrodynamic phenomenon known as localized surface plasmon resonance (LSPR) which is generated by the collective oscillation of free electrons of nanoparticles in response to a characteristic electromagnetic excitation whose wavelength is larger than the nanoparticle diameter. As a result noble metal nanoparticles are emerging as key materials for catalysis,[1] plasmonic sensing,[2] biological imaging and medical therapeutics.[3] The LSPR frequency of noble metal nanoparticles strongly depends on size, shape, crystallinity and assembly, but also on the local environment of the nanostructures, including substrate, solvent and capping agent.[4–6] A complete control of the reaction is, therefore, compulsory in order to tailor their properties for a specific application. As a result, intensive research is being carried out on the synthesis of these nanometer-sized materials. Metal nanoparticles have been synthesized by various techniques, mainly based on the chemical reduction of metallic ions in aqueous or organic solvents.[7–11] Traditionally, chemical reduction of silver and gold salts has been carried out by heating the reagent solutions. Conventional oil-bath heating by conduction and convection results in non-homogeneous temperatures within the solvent. Microwave (MW) dielectric heating has also been applied to the synthesis of metallic nanoparticles because it provides rapid and uniform heating of reagents, solvents, and intermediate/final products.[12,13] Fast heating accelerates the reduction of metal precursors and the nucleation of the metal cluster, resulting in monodispersed small nanostructures. The principle of MW heating of polar molecules is based on the conversion of this radiation energy into thermal energy by dielectric losses. In the microwave frequency range, polar molecules try to orientate along the electric field. When the dipolar moment of molecules tries to follow the direction of an alternating electric field, they lose energy in the form of heat by molecular friction. The ability of a medium to absorb microwave irradiation and convert it into heat is determined by the tangent loss ($\tan\delta = \varepsilon''/\varepsilon'$), which depends on the dielectric constant (ε') and the dielectric loss (ε'') of the solvent. Both constants, ε' and ε'', will depend on the solvent, temperature and MW frequency.[12] A reaction medium with a high $\tan\delta$ is required for efficient absorption and consequently for rapid heating, making the choice of the reaction important in MW-assisted synthesis. Microwave heating methods can therefore address the problem of heating-inhomogeneity, while providing a scalable platform for industrial applications. In fact, microwave heating has been demonstrated to enhance reaction rates, selectivity and product yields in organic chemistry.[14]

Here, we report a novel synthetic route to form colloidal Ag and Au nanoparticles. This method is based on the MW-assisted reduction of $AgNO_3$ and $HAuCl_4$ by means of PVA. The reaction is carried out in short-chain alcohols ($\tan\delta > 0.5$), which are non-solvents for PVA. As a result, the formation of Ag and Au nanoparticles occurs very fast through a heterogeneous process. The resulting Au and Ag nanoparticles are very easily purified and separated by filtration to finally obtain a powder. Further addition of hot water results in a stable and transparent colloidal solution. Moreover, size-controlled formation of nanoparticle agglomerates can be accomplished with a seed-mediated synthesis of nanoparticles in $MeOH–H_2O$ upon MW exposure. As a result, strong plasmon coupling was observed with increasing reaction time. These could be used for extending plasmon resonance effects towards the red and the NIR. This has potential applications in several fields, such as photothermal-nanotherapy induced by light-absorption, similar to the use of metal nanoshells.[15]

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Experimental

Materials and apparatus

Polyvinyl alcohol (PVA), silver nitrate ($AgNO_3$), $HAuCl_4$ and the solvents used in the study, such as methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH), 2-propanol (IPA) and *tert*-butanol (*t*-ButOH), were purchased from Aldrich and used as received. The apparatus used for the preparation was a domestic MW oven (1000 W, 2450 MHz).

Preparation of silver colloids and agglomerates-

The synthesis of Ag nanoparticles was carried upon MW exposure at 300 W from an initial suspension of PVA in an alcoholic solution of $AgNO_3$ or $HAuCl_4$. The reaction took place in a closed vial. Water was added and a colloidal solution of Ag nanoparticles obtained. For the preparation of silver agglomerates an $AgNO_3$ aqueous solution was added to a seed solution of Ag–PVA nanoparticles in MeOH–H_2O and exposed to MW irradiation.

Experimental techniques

Ultraviolet-visible (UV-Vis) spectroscopy (Perkin-Elmer Lambda 20 spectrophotometer) was used to follow the reaction process and to characterize the optical properties. Light transmission was measured through quartz cuvettes of 1 cm light-path. The X-ray diffraction patterns (XRD) were recorded on a Shimadzu XD-3A X-ray diffractometer using Cu Kα radiation ($\lambda \sim 0.15418$ nm) operated at 50 kV and 100 mA. Transmission electron microscopy (TEM) was performed with a Hitachi 600 microscope operating at 100 kV. The diameter of around 400 nanoparticles was measured for each sample to obtain a representative size-distribution.

Results and discussion

PVA has already been reported to reduce Ag(I) and Au(III) and is considered a mild reducing agent.[7,16,17] The polyol process is a popular method for the synthesis of metal nanoparticles. Ethylene glycol is often employed for the reduction of metal ions to form the nanoparticles.[10] Unlike that synthetic procedure, the method here-described occurs through a heterogeneous process. The reaction is carried out in alcohols in which PVA is insoluble, but can be well-dispersed. Alcohols are considered an appropriate solvent for MW-assisted synthesis due to their high tan δ. Synthesis of silver and gold nanoparticles was confirmed by UV-Vis spectroscopy. As can be seen in Fig. 1a, typical surface plasmon resonances of Ag and Au nanoparticles are observed at a wavelength of around 400 and 520 nm, respectively. The XRD patterns corresponding to silver and gold nanoparticles are shown in Fig. 1b. The measured diffraction peaks are attributed to (111), (200), (220), and (311) planes by using approximately the lattice parameter for both bulk silver and gold, which means that face-centered cubic crystalline nanoparticles are obtained with the proposed synthesis method. The diffraction peak found at 40.6° corresponds to PVA crystalline phase.[18]

Fig. 1c–d show TEM images of PVA-coated Au and Ag nanoparticles prepared in methanol and their corresponding size-distributions. Most of the silver and gold nanoparticles obtained upon MW irradiation are spherical, although a few faceted nanocrystals are observed in gold colloids. The average diameters of Ag and Au nanoparticles are very similar, about 10.4 and 11 nm, respectively.

The MW-assisted reduction of Ag(I) and Au(III) with PVA is carried out from an initial suspension of PVA in a methanolic solution of the corresponding metal salt. After only 30 s, a yellowish and reddish turbid suspension of Ag–PVA and Au–PVA nanoparticles, respectively, are obtained, which turn to a stable colloidal solution after water addition (their LSPR spectra were shown in Fig. 1a). PVA acts simultaneously as reducing and capping agent. When a solution of PVA and $AgNO_3$ in ethanol–water 1 : 1 was irradiated with MW, Ag nanoparticles are also obtained, but exhibiting a very broad LSPR peak, as shown in Fig. 1a (circles), due probably to nanoparticle coalescence during the MW irradiation. Indeed longer MW exposure times (120 s) are necessary in order to obtain the nanoparticles. This simple experiment confirms that Ag(I) reduction with PVA is significantly improved when PVA is in suspension rather than in solution.

The reduction mechanism of Ag(I) and Au(III) in this system may take place as follows. In the first stage, PVA is dispersed in an alcoholic solution of $AgNO_3$ or $HAuCl_4$. After agitation, the OH groups of the suspended PVA molecules, which are in contact with the Ag(I) and Au(III) solution, produce the complexes Ag^+ and $AuCl_4^-$. Upon MW irradiation exposure, some of these ROH groups are oxidized to the corresponding ketone, thus reducing Ag(I) and Au(III) to Ag(0) and Au(0) respectively. This reduction should occur on the surface of the PVA particles in suspension in the non-solvent through a heterogeneous reaction. Ultrasonication prevents the aggregation of PVA into large particles within the non-solvent and facilitates the complex formation of more Ag(I) and Au(III). As a result, the PVA active sites increase and reaction kinetics accelerated.

One of the main characteristics of our proposed synthesis method is that the metal reduction takes place very fast and can be scalable for massive production. Fig. 2 shows the dependence of Ag nanoparticle formation on the MW exposure time. We observe that the main part of the reaction, 85%, takes place within the first 10 s and it is practically finished after 30 s, as better observed in the inset of Fig. 2. The evolution of the reaction shows a sigmoidal curve with three different main regions. This is indicative that the kinetics of the MW-assisted Ag(I) reduction follows a typical autocatalytic behavior.[19,20] During the first 3 s, a slow induction phase took place. We assume that during this time Ag nucleation occurs, which does not result in a significant increase in the absorbance. Above 3 s of MW irradiation, we observe a dramatic increase in absorbance due to the autocatalytic reduction of Ag(I) on pre-existing Ag nuclei. After this region of drastic increase, absorbance reaches a constant saturation value, since the reaction is nearly finished. It must be taken into account that the reaction takes place in a closed vial. As a result, the pressure increases upon MW exposure, which obviously contributes to accelerate the reaction kinetics.

The role of the non-solvent in the reaction was also investigated. Several water-miscible alcohols such as MeOH,

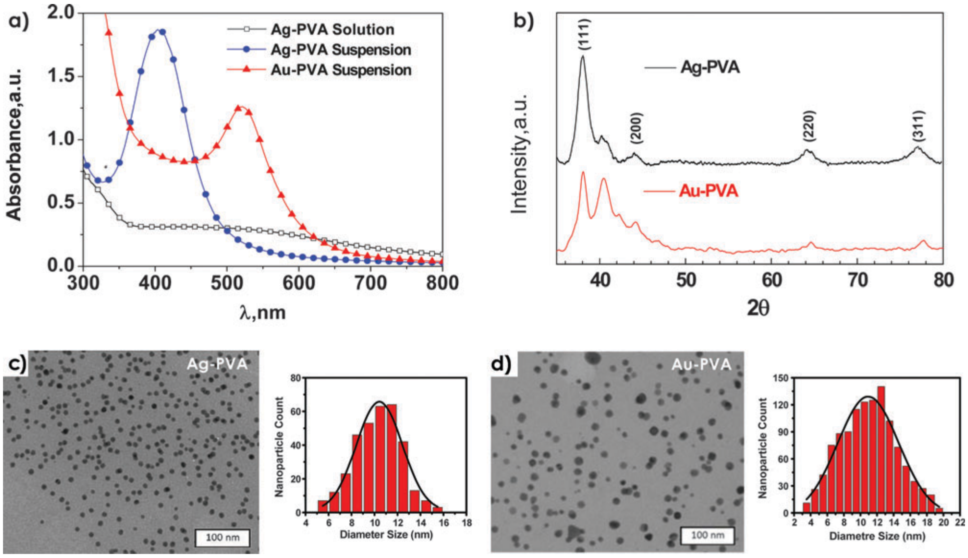

Fig. 1 Characterization of Ag and Au nanoparticles. (a) Absorption spectra, (b) RX diffractogram, (c) Ag–PVA and (d) Au–PVA TEM images and size distributions.

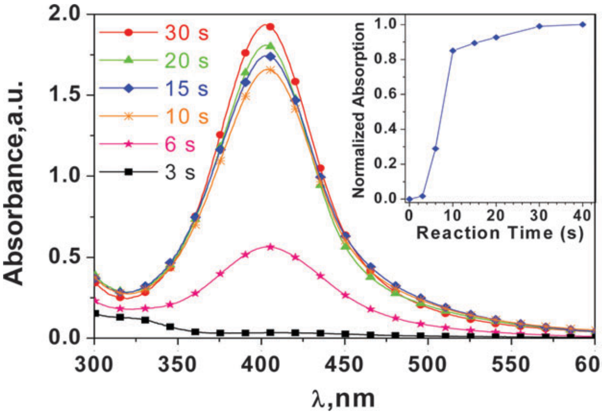

Fig. 2 Absorption spectra of Ag nanoparticles for different MW irradiation times (the inset shows the variation of the LSPR intensity as a function of the MW exposure time.

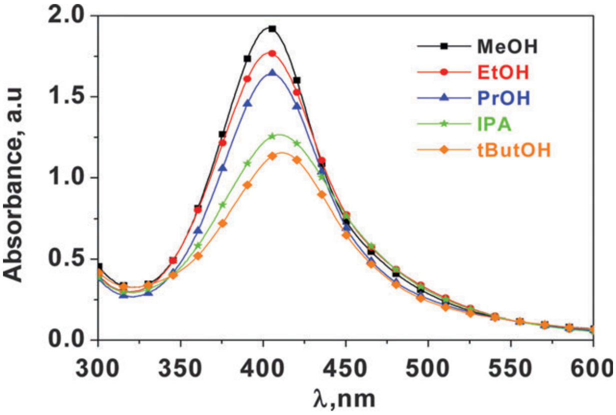

Fig. 3 Absorption spectra of Ag nanoparticles for different non-solvents on the reaction.

EtOH, PrOH, IPA and *t*-ButOH were tested upon MW exposure of 30 s. The use of different non-solvents influences the MW-assisted synthesis of Ag nanoparticles, as can be observed in Fig. 3.

Among the studied low molecular weight alcohols, MeOH reached the highest LSPR peak intensity in the resulting colloid, even if very similar to that in the colloids obtained from EtOH and PrOH alcohols. More significant differences are observed in the case of silver nanoparticles synthesized in IPA and *t*-ButOH non-solvents, for which we observe a 50% reduction in the LSPR peak intensity and a wavelength red-shift from 404 to 411 nm. The intensity differences are attributed to a decreasing efficiency of the reduction reaction when increasing the molecular weight of the non-solvent alcohol, from MeOH to *t*-ButOH. The wavelength red-shift, especially important in colloids obtained when using IPA and *t*-ButOH, is attributed to the dielectric medium surrounding the nanoparticles,^{6} mainly PVA, the different alcohols and the amount of unreacted Ag(I) ions, the size of the nanoparticles being very similar in all cases (see Table 1 and Fig. 4), as shown below.

One could think that the different reaction extent reached with alcohols might in principle depend on their physical parameters, which are listed in Table 1. The boiling temperature of non-solvents being a factor to take into account, tan δ is the most important physical parameter, since it is related to the ability of a medium to absorb microwave irradiation and convert it into heat. All the solvents used have a relatively high value of tan δ (>0.5), which makes them suitable

Table 1 Physical properties of the alcohols tested (Data taken from ref. 21) and average particle size of Ag nanoparticles prepared from different alcohols

Alcohol	Boiling point/°C	Tan δ	1st size/nm	2nd size/nm
Methanol	64	0.66	—	10.4 ± 1.9
Ethanol	78	0.94	7.4 ± 0.8	10.2 ± 1.2
1-Propanol	97	0.76	7.0 ± 1.2	10.3 ± 1.4
2-Propanol	82	0.80	6.1 ± 1.7	10.1 ± 3.1
tert-Butanol	82	<0.5	5.8 ± 1.6	—

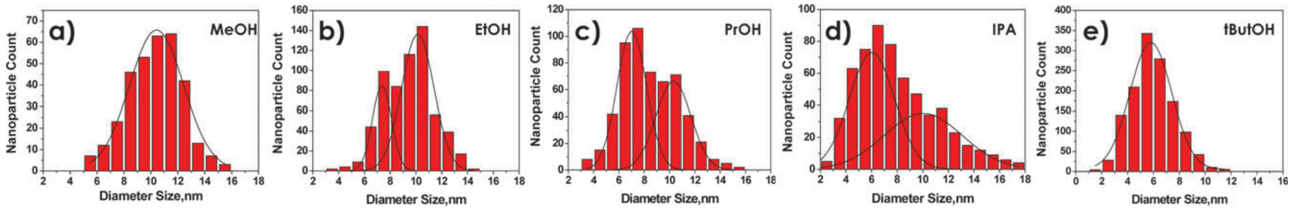

Fig. 4 Size distribution histogram of Ag–PVA nanoparticles prepared from (a) MeOH, (b) EtOH, (c) PrOH, (d) IPA and (d) *t*-ButOH alcohols.

solvents for MW-assisted synthesis. However, MeOH shows the best results in spite of having both the lowest boiling temperature and the second lowest value of tan δ. This can only be explained by the different chemical properties of alcohols. We observed that the best LSPR intensity values were measured with primary alcohols having the smaller chain length (MeOH, EtOH and PrOH), followed by secondary (IPA) and tertiary (*t*-ButOH) alcohols. Primary alcohols can be oxidized to aldehydes and carboxylic acids, whereas secondary alcohols only to ketones. Tertiary alcohols do not react to give any oxidation products as they have no H attached to carbon that is bonded to the hydroxyl group. Therefore, *t*-ButOH is an inert non-solvent which is useful to know the real capacity of PVA as a reducing agent to produce metal nanoparticles.

Fig. 4 shows the histograms of the NP size distributions of Ag–PVA colloids prepared from different alcohols (mean diameters are also listed in Table 1). We observe that Ag nanoparticles prepared from EtOH, PrOH and IPA (Fig. 4b, c, and d) exhibit a bimodal size distribution, whereas those prepared from MeOH and *t*-ButOH (Fig. 4a and e) are nicely represented by a single mode size distribution. This behaviour is related to the difference between the reducing properties of alcohols. As suggested above, both PVA and alcohols are involved in the reduction of Ag(I). In the two limits of the studied alcohols, from primary to tertiary alcohols, we observe that nanoparticles prepared from *t*-ButOH (size mode 1), where Ag(I) reduction is only carried out by PVA, exhibit the smallest mean diameter, 5.8 nm, whereas nanoparticles obtained with MeOH (size mode 2), the most reactive alcohol, show the largest mean diameter of 10.4 nm. For the other alcohols we detect both size modes, but mode 2 (mode 1) increasing (decreasing) in importance when rising reactivity of the non-solvent (EtOH > PrOH > IPA). We can say that the Ag(I) reduction reaction is completely exhausted when using MeOH and nanoparticles cannot further grow above the average 10.4 nm value.

In order to obtain larger nanoparticles we propose a seed-mediated reduction of Ag(I) using the colloidal Ag–PVA nanoparticles prepared from methanol (d = 11 nm) as a seed solution. Fig. 4a shows the LSPR spectra obtained after mixing an growth aqueous solution containing silver salt to the nanoparticle seed solution upon different MW irradiations. After the addition of Ag(I) we observe a slight increase of the LSPR intensity upon non-MW exposure. This is attributed to the autocatalyzed growth of the Ag nanoparticles on pre-existing seeds: the activation energy for metal reduction onto an already formed particle is significantly lower than for homogeneous nucleation of seed particles in solution.[22] Upon a MW exposure of only 5 s the absorbance spectrum changes significantly and two resonances appear, as observed in Fig. 5a. The first plasmon resonance is slightly blue-shifted from 405 nm to 399 nm and decreases in intensity with longer MW exposure times, whereas the second plasmon resonance increases in intensity and red-shifts up to 650 nm for increasing the MW exposure time. As a result, the as-synthesized colloidal silver nanoparticles absorb from 350 to 800 nm, this is, from the near-UV to the NIR. This effect can be primary attributed to either the formation of non-spherical nanoparticles[4,5] or the plasmon coupling among nanoparticles in agglomerates.[6,23] Fig. 5b and c show TEM images of the seed-mediated Ag–PVA colloids synthesized upon MW exposure of 15 and 50 s, respectively. Firstly, we notice a significant increase of the nanoparticle size with respect to seed nanoparticles: from 11 to 22 nm, with non-spherical shapes. Secondly, we observe the formation of nanoparticle agglomerates, from small linear chains to random morphologies of increasing size when increasing the MW exposure time. The very small interparticle distances in these agglomerates, even inexistent in some cases, allow the plasmon coupling between them. This gives rise to the low

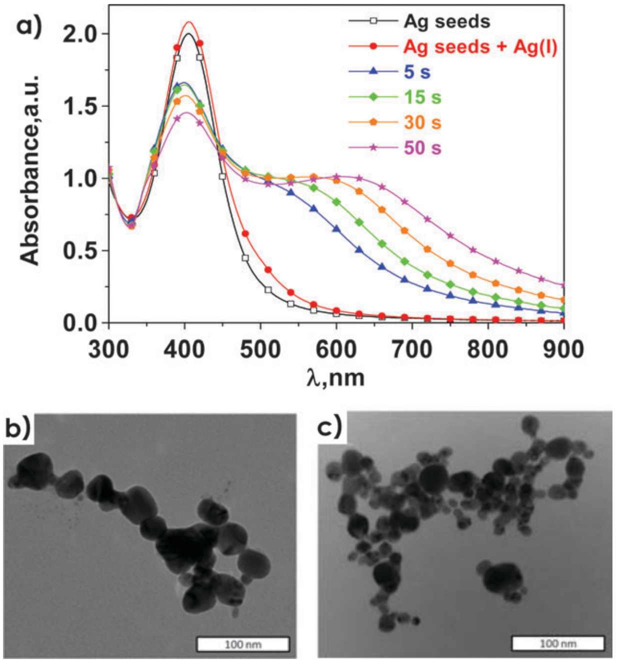

Fig. 5 Seed-mediated synthesis of Ag nanoparticles. (a) Absorption spectra of Ag nanoparticles upon different MW exposure. (b) and (c) TEM images of Ag–PVA agglomerates prepared upon MW exposure of 15 and 50 s, respectively.

energy LSPR mode observed in Fig. 5a, which is more noticeable with increasing agglomerate size.

Conclusions

In the present work, we report a new synthetic route to form colloidal Ag and Au nanoparticles. This method is based on the reduction of $AgNO_3$ and $HAuCl_4$ upon MW irradiation by means of PVA in short-chain alcohols. The reaction is carried out through a heterogeneous reaction because alcohols are non-solvents for PVA. As a result nanoparticles are very easily purified and separated by filtration. Moreover, the reaction kinetics is especially very fast since upon exposures of only 30 s the reaction is finished. We observed that reduction shows an autocatalytic behavior. The influence of non-solvent on the nanoparticle synthesis was also investigated. Best results were achieved with primary alcohols with lower chain length. We observed that both alcohols and PVA play an important role on the reduction of Ag(I). Growth of larger nanoparticles as well as agglomerate formation was accomplished with an initial seed-mediated synthesis in MeOH–H_2O upon MW exposure. Strong plasmon coupling was observed with increasing reaction time and agglomerate size.

Acknowledgements

The authors gratefully acknowledge financial support by the Generalitat Valenciana (IMPIVA-IMCITA/2007/02 and IMPIVA-IMIDIN/2008/16) and the Spanish Ministry of Science through project TEC-2005-05781-C03-03.

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