

A novel synthetic route for preparation of Ag nanoparticles in aqueous emulsion of copolymer template

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We report on a novel synthetic route for preparing of Silver nanoparticles inside polymer matrix by solid-state chemical reduction of a metallic salt silver nitrate (AgNO_3 , 99%) under microwave irradiation. The reaction has been performed in an emulsion of copolymers with the presence of ethanol to reduce Ag (I) to the corresponding nanoparticle. The nanoparticle diameters of Ag were found to be from 4 to 12 nm. TEM also indicated uniform distribution of nanoparticles embedded in the thin film. This approach is more suitable for controlling the nanoparticle size and their homogeneous distribution in the polymer matrix. The effect of Microwave irradiation duration on the reaction rate was investigated by transmission electron microscopy, UV-visible and RX analysis.

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1. Introduction

Metal nanoparticles have attracted a great attention in last recent years due to the quantum –confinement effect on their electronic, optic, magnetic and other relevant properties. Noble metal nanoparticles such as Ag, Au and Cu possess a very strong absorption in the UV and visible spectrum. These optical properties are related to localized surface plasmon resonance involved by the collective oscillation of free electrons of nanoparticles in response to a characteristic electromagnetic excitation whose wavelength is larger than the nanoparticle diameter.

These properties are used in plasmonic sensing [1], biological imaging [2] and medical therapeutics [3]. The resonance frequency of noble metal nanoparticles strongly depends on size, shape, and on the local environment of the nanostructures.

Metal nanoparticles have been synthesized by various techniques, mainly based on the chemical reduction of metallic ions in aqueous or organic solvents. [4,5] Traditionally, chemical reduction of silver salts has been carried out by heating the reagent solutions.

Conventional 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. [6,7] The principle of MW heating of polar molecules is based on the conversion of this radiation energy into thermal energy by dielectric losses. The ability of a medium to absorb microwave irradiation and convert it into heat is determined by the

tangent loss ($\tan \delta = \epsilon''/\epsilon'$), which depends on the dielectric constant (ϵ') and the dielectric loss (ϵ'') of the solvent. Both constants, 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.

Several polymers such as poly (ethyleneimine) (PEI), Poly (hydroxy ethylmethacrylate) (PHEMA), Poly (vinyl pyrrolidone) (PVP), Novolac, poly(4-vinylphenol) (P4VP), Poly(4-vinylphenol)-co-(methylmetacrylate) (P4VP-co-MMA) and poly (styrene-co-allyl alcohol) (PS-co-AA) are considered ideal candidates as host polymers since they combine good processing capabilities (high solubility in many solvents), and excellent film forming characteristics. Furthermore, these polymers possess certain functional groups able to produce the in-situ reduction of Ag(I) and Au(III) salt to the corresponding nanoparticles.

Here, we report a novel synthetic route to form colloidal Ag nanoparticles. This method is based on the MW-assisted reduction of AgNO_3 by means of an aqueous emulsion of copolymer. The reaction is carried out in short-chain alcohols ($\tan \delta > 0.5$). Moreover, size-controlled formation of nanoparticle agglomerates can be accomplished with a seed-mediated synthesis of nanoparticles in Ethanol 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.

Aqueous emulsions are heterogenic phase systems in which stable nanodroplets of one phase are dispersed in a second, continuous phase polymer particles prepared as synthetic emulsions and latexes are frequently applied as binders in the industrial fields of paint, paper and inks, and films such as adhesives and coating materials.

Those emulsions are prepared of nano to micron-sized polymer particles by radical polymerization of vinyl monomers in environmentally friendly heterogeneous aqueous media. Consequently considerable attention has recently been directed towards aqueous dispersed systems due to the increased awareness of environmental issues.

Moreover, such polymer particles have already been applied to more advanced fields such as biotechnology where latexes have many potential biomedical applications such as controlled-release drug-delivery [8,9], biocatalysis applications [10,11]. Fluorescent-dyed latex particles [12] are also used in fluorescence microscopy, and DNA analysis applications.

In the field of electronic technologies interest of latex in nanofabrication is increasing in designing regular structures in the nanoscale range which have relevant optical [13] and electrical [14] properties for optoelectronic devices such as sensors [15].

Nanostructured materials [16] can be produced using latex particles as templates to obtain a nano size polymer particles with uniform diameters which are arranged into regular structures upon drying [17].

In addition to the commercial interest of latex and emulsion, it is of fundamental scientific interest to elucidate the interest of those systems related to the fact that each of the nanodroplets can be regarded as a nanoscopic, individual batch reactor. A whole variety of synthesis reactions at the nanometric scale can be performed in this kind of medium. Additionally, aqueous emulsions are also suited for the encapsulation of various solid or liquid materials.

Emulsion polymers are colloids, meaning that they consist of small, discrete particles dispersed in a continuous liquid media. Colloids have many unique and interesting properties as a result of their small size (typically less than 1 μ m and large interfacial area (typically greater than 104 cm²/cm³ latex) [18].

The interfacial free energy increase is substantial in colloids with small sizes and large interfacial areas. The minimisation of interfacial free energy is thermodynamically favorable [19], and provides a strong driving force for coagulation. Droplets reduce interfacial area by coalescence into pools of monomer, and particles do so by aggregation) into masses of polymer (coagulum) [20,21].

In this work we have sought to combine the advantages of the chemical reduction route to metal nanoparticles, environment- friendly reagents, and the stabilization of the particles in a latex matrix, in the fabrication of silver nanoparticles embedded in polymer dielectric films. Our goal was to use of latex as commercial ship medium in the nanoparticle fabrication combined to the valorization of latex widely applied in industrial field of paint and thermal insulating.

2. Experimental

2.1 Materials and apparatus

The aqueous emulsion of Copolymer (latex), silver nitrate (AgNO₃, 99%), the solvent used in the study is ethanol (EtOH). The apparatus used for the preparation was a microwave oven Mars5 (System from company CEM).

2.2 Preparation of silver nanoparticles

In a typical synthesis, latex (0.10 g) was dissolved in Ethanol (25 ml) under magnetic stirring in order to obtain a colourless transparent latex solution. A solution of silver nitrate-ethanol (2mM, 25 ml). The synthesis of Ag nanoparticles was carried upon MW exposure at 300 W. Under these reaction conditions, the apparent colour in the resulting sample Ag-latex (consists of derived Ag-metal nanoparticles, which are dispersed and embedded in the Copolymer latex matrix) deepens gradually from an achromatic colour in the beginning to a faint yellowish equilibrium colour. In order to retain a stable Ag-latex colloid structure, which consists of Ag nanoparticles capped in latex molecules, the sample was cooled at 20–25°C temperature just after the reaction.

2.3 Characterization techniques

Transmission electron microscopy (TEM) studies of the particles were carried out at an accelerating voltage of 120 kV using a FEI TECNAI G microscope. TEM samples were prepared by a deposit of a micro droplet of the solution on a copper grid, after the vaporisation of the solvent we obtained micrometric pieces of the corresponding nanocomposites thin film. The solution containing nanoparticles was characterized by UV-VIS spectroscopy (spectrophotometer UV-3100 selecta) to correlate their optical properties with the size, shape of nanoparticles and their particle dispersion in the polymer matrix. The X-ray diffraction patterns (XRD) were recorded on BRUKER (ADVANCE D8) diffractometer using Cu K α radiation (λ ~0.15418 nm) operated at 50 kV and 100 mA.

3. Results and discussion

Polymers has already been reported to reduce Ag (I) and is considered a mild reducing agent [4, 22, and 23]. The polyol process is a popular method for the synthesis of metal nanoparticles.

Our new synthesis approach differ significantly to the traditional one, in the place of simple polymer we use an aqueous emulsion of copolymers.

The method here-described occurs through a heterogeneous process. The reaction is carried out in alcohol.

Alcohols are considered an appropriate solvent for MW-assisted synthesis due to their high $\tan\delta$. Synthesis of silver nanoparticles was confirmed by UV-Vis spectroscopy. As can be seen in Fig. 1a, typical surface plasmon resonance of Ag nanoparticles is observed at a wavelength of around 425 nm. The formation of Ag nanoparticles after thermal treatment in the latex matrix is also confirmed by X-ray diffraction analysis (Fig. 1b). All

the prominent peaks at 2θ values of about 38.38° , 44.56° , 64.82° , 77.77° representing the (111), (200), (220), (311) Bragg's reflections of fcc structure of silver [24].

Fig. 1c show TEM image of Copolymer-coated Ag nanoparticles prepared in ethanol and their corresponding size-distribution. Most of the silver nanoparticles obtained upon MW irradiation are spherical. The average diameter of Ag nanoparticles are about 7 nm.

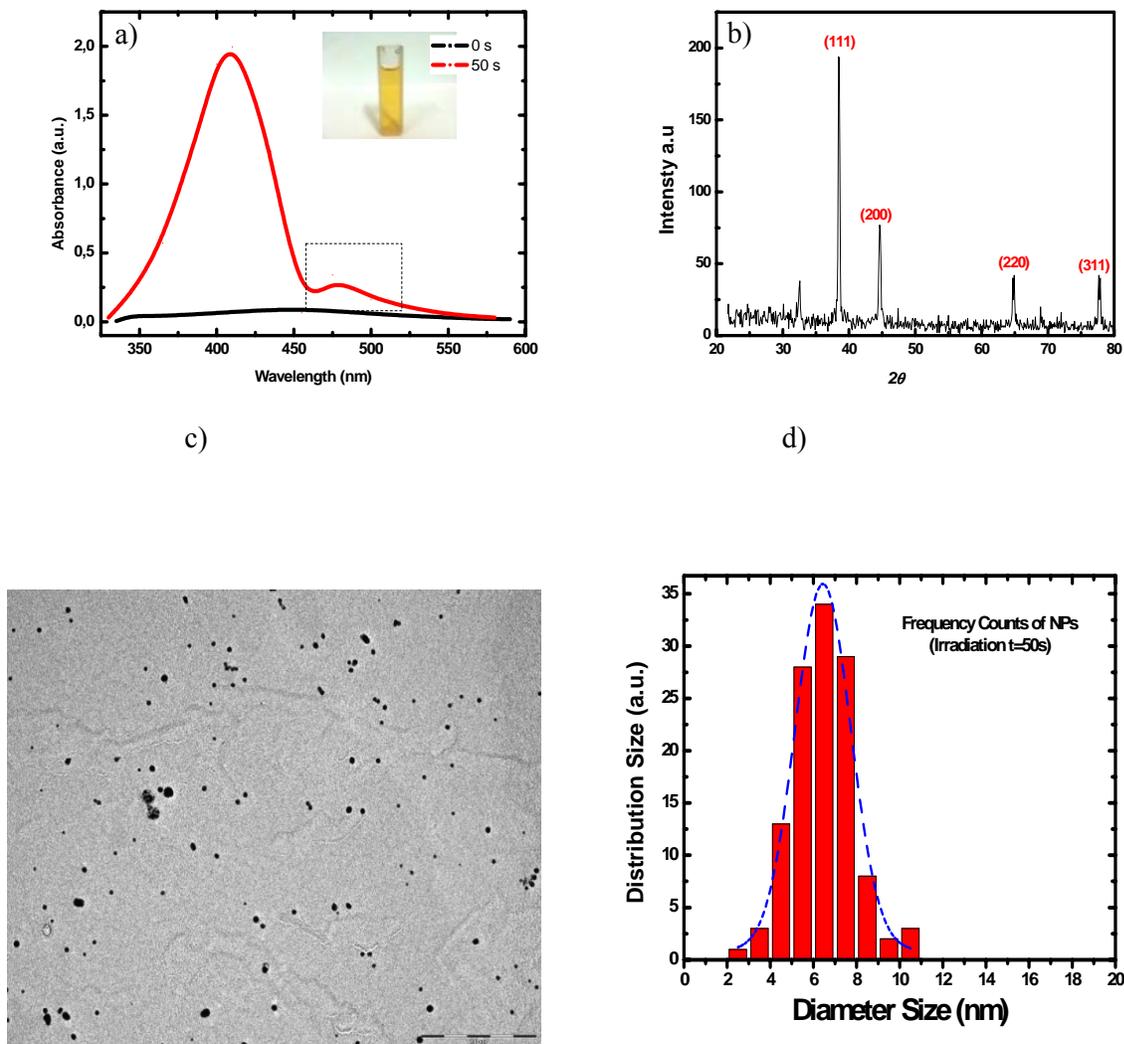


Fig. 1. Characterization of Ag nanoparticles. (a) Absorption spectra, (b) RX diffractogram, (c) Ag-Copolymer TEM image and (d) size distribution.

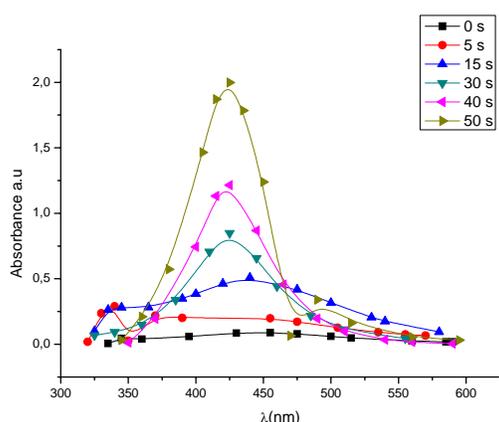
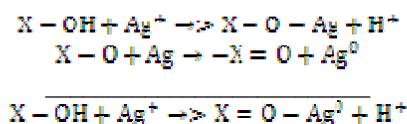


Fig. 2. Absorption spectra of Ag nanoparticles for different MW irradiation times.

The MW-assisted reduction of Ag (I) with copolymer is carried out from an initial suspension of copolymer in an ethanolic solution of the corresponding metal salt. After only 50 s, a yellowish suspension of Ag– Copolymer nanoparticles (their LSPR spectra were shown in Fig. 1a). Copolymer acts simultaneously as reducing and capping agent. When a solution of copolymer and AgNO₃ in ethanol was irradiated with MW, Ag nanoparticles are also obtained, but exhibiting a very broad LSPR peak, as shown in Fig. 1a (dash line), due probably to nanoparticle coalescence during the MW irradiation.

The reduction mechanism of Ag (I) in this system may take place as follows. In the first stage, copolymer is dispersed in an alcoholic solution of AgNO₃. After agitation, the OH groups of the suspended copolymer molecules, which are in contact with the Ag(I) solution, produce the complexes Ag⁺. Upon MW irradiation exposure, some of these X-OH groups are oxidized to the corresponding ketone, thus reducing Ag(I) to Ag(0). This reduction should occur on the surface of the copolymer particles in suspension, the mechanism reported as follows:



Here, X-OH represents a polymer monomer, X=O represents a monomer in a partially oxidized polymer. 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 nanoparticles formation on the MW exposure time. We observe that the main part of the reaction, 85%, takes place within the first 30 s and it is practically finished after 50 s.

This is indicative that the kinetics of the MW-assisted Ag(I) reduction follows a typical autocatalytic behavior. [25,26] During the first 5 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 5 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 reactor (HP500). As a result, the pressure increases upon MW exposure, which obviously contributes to accelerate the reaction kinetics.

4. Conclusion

The formation of silver nanoparticles in aqueous emulsion of copolymer (latex) which act as stabilized agent has been described. The process of silver ions entrapment in the emulsion and their in situ reduction results in the formation of silver nanostructures of variable morphology in the emulsion. This morphology variation in the silver nanocrystals is believed to occur due to differences in the structure of the emulsion, which varies from highly anisotropic to extended isotropic one. A combination of extremely large interfacial templating area provided by the liquid lamellae in dispersible polymers makes this method potentially exciting for the large-scale synthesis of other nanomaterials.

In summary, a novel simple method for preparing Ag nanoparticles by reducing AgNO₃ with ethanol in aqueous emulsion of copolymer under microwave irradiation has been developed. Nonagglomerated and stably suspended Ag nanoparticles in colloidal solution are obtained. The results shows that the addition of copolymer suspension and the adoption of microwave irradiation greatly affect the reaction rate and the properties of Ag nanoparticles. It is expected that this method can first be a more sheep template and efficient method of preparing Ag nanoparticles, second provide a new challenge of changing optical and thermal properties of latex which is one of product largely used in industry.

We have sought to combine the advantages of the chemical reduction route to metal nanoparticles, environment- friendly reagents, and the stabilization of the particles in a latex matrix, in the fabrication of silver nanoparticles embedded in polymer dielectric films. Our goal was to use of latex as commercial ship medium in the nanoparticles fabrication combined to the valorization of latex widely applied in industrial field of paint and thermal insulating.

To the best of our knowledge, this is the first report of in situ fabrication of nanoparticles in a dispersive emulsion. Further, our methodology opens up a wide range of possibilities in terms of the choice of metals, polymers, and particle growth conditions and the feasibility.

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