Controlled Size Gold Nanoparticles Obtained by Tuning Synthesis Parameters in Microemulsion Templates

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The technique developed in this study combines microemulsion as one of soft-nanotechnology techniques of wet chemistry with photo-physics of UV-radiation into a unique versatile method to design and obtain controlled nanostructures for multifunctional materials. The UV photo-induced reduction of Au(III) in a series of water in oil microemulsions produced homogeneous spherical particles with various diameters ranging between 2.5 and 30 nm, depending on the oil type used. The gold nanoparticles size can be also tuned by this route, using different initial concentrations of Au(III) precursor of 1, 5 and 10 g/L. The obtained diameters are 10, 45 and 75 nm. The evolution of the system at nanoscale has been followed, using in tandem, by parallel and successive UV-Vis and DLS measurements, while the structure, size and shape of final nanoparticles obtained have been demonstrated by TEM image analysis. Kinetic studies have been also performed in order to follow the evolution of nanospecies during irradiation procedure. A new, clean, cost effective and rapid method for the synthesis of stable spherical gold nanoparticles (AuNPs) is developed.

Keywords: gold nanoparticles, photoreduction, microemulsion, size controlled

The physico-chemical properties of nanomaterials are strongly affected by their shape and size [1–5]. In the research of nanomaterials many strategies have been developed for shape and size controlled synthesis of metallic nanoparticles, including vapour phase techniques [6], sol-gel methods [7], sputtering [8], coprecipitation [9], photo-induced synthetic method [10-16], microemulsion assisted chemical reduction [17-24], etc.

For the size controlled synthesis of nanoparticles, besides the above traditional methods, the microemulsion assisted photoreduction (MAPR) method has been developed recently [25]. This procedure benefits of the advantages of microemulsion templates, while at the same time, uses light as an efficient tool for metallic cation reduction. Thus, very important features can be obtained, such as: (i) advantageous properties of the photoinduced processing, meaning a clean process, high spatial resolution, and convenient useful, (ii) controllable *in situ* generation of reducing agents with formation of nanoparticles which can be triggered by the photoirradiation, and (iii) a great versatility because the photochemical synthesis enables to fabricate nanoparticles in both water-in-oil (W/O) and oil-in-water (O/W) microemulsion systems increasing the experimental flexibility of this method to confine at nano-scale both hydro- and liposoluble components; iv) this method can be modified at a high extent by adjusting the type or ratio of polar/nonpolar phase and surfactants, thus allowing fine adjustment of the micelles and nanoparticles diameter; v) as nanoparticles-containing microemulsion is a very stable suspension and metal precursor reduction does not require any reducing agents, the final product can be used in suspension without further treatments.

Almost monodisperse metal nanoparticles can be obtained by controlled nucleation and separation of nucleation centers on growth by using microemulsion templates. The size of the final metallic nanoparticles will depend mostly on the size of the droplets in microemulsion. Therefore, the selection of adequate microemulsion system is very important from the particles preparation and application point of view [26].

In this paper, different water-in-oil (W/O) microemulsion systems have been evaluated for gold nanoparticles (AuNPs) preparation using UV light as an efficient tool for metallic cations reduction. The effect of gold precursor concentration on the nanoparticles size and their aqueous dispersion stability has also been investigated.

Experimental part

Materials

Hydrogen tetrachloroaurate ($HAuCl_4$), polyoxyethylene 4-lauryl ether (Brij 30), ciclohexane (C6), n-heptane (C7), iso-octane (i-C8), nonane (C9), iso-propanol (C3), ethyl acetate (ETAC) and polyethylene glycol (PEG) were purchased from Sigma–Aldrich. All chemicals were of analytical grade and used without further purification. Ultra-pure water (Millipore Corporation) was used.

Procedure

A series of water-in-oil microemulsion systems with the variation of organic phase nature have been tested in order to obtain gold nanoparticles with various sizes: ETAC/Brij30/$HAuCl_4$, C6/Brij30/$HAuCl_4$, C7/Brij30/$HAuCl_4$, i-C8/Brij30/$HAuCl_4$, C9/Brij30/$HAuCl_4$. For the evaluation of gold precursor concentration effect on the nanoparticles size and their aqueous dispersion stability, different Au(III) aqueous solutions, in the range of $1 \div 10$ g/L, using C7/Brij30/$HAuCl_4$ microemulsion template have been prepared. Kinetic studies on photoreduction reaction of Au(III), using the last system as template, have been also performed. For each Au(III) concentration, 1, 5 and 10 g/L, at different irradiation time (10, 30, 60, 120, 180, 240, and 360 min), UV-Vis spectra and dynamic light scattering (DLS) measurements (size and Zeta potential) have been used for investigation. All measurements were carried out on AuNPs dispersed in microemulsion.

A photoreactor with a mercury lamp that primary emits at 254 nm (14 W) was used.

Gold nanoparticles have been synthesized by using a method previously discussed [25], and reported as microemulsion assisted photoreduction (MAPR) technique.

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Table 1
SIZE GOLD NANOPARTICLES DEPENDENCE ON MICROEMULSION TEMPLATE

Microemulsion template	AuNPs	
	Size, nm	*Pdl*[a]
ETAC/Brij30/$HAuCl_4$	2.5	0.21
C6/Brij30/$HAuCl_4$	24.1	0.20
C7/Brij30/$HAuCl_4$	9.8	0.25
i-C8/Brij30/$HAuCl_4$	30.0	0.30
C9/Brij30/$HAuCl_4$	18.0	0.40

a. Pdl–Polydispersity

Table 2
AQUEOUS DISPERSION STABILITY OF GOLD NANOPARTICLES

Microemulsion template	Aqueous dispersions of AuNPs		
	Size, nm	*Pdl*[a]	*ZP*[b], mV
ETAC/Brij30/$HAuCl_4$	15.1	0.5	15.2
C6/Brij30/$HAuCl_4$	52.6	0.4	26.5
C7/Brij30/$HAuCl_4$	11.0	0.3	22.5
i-C8/Brij30/$HAuCl_4$	95.0	0.5	25.0
C9/Brij30/$HAuCl_4$	30.4	0.4	28.7

b. Zeta potential

Table 3
AQUEOUS DISPERSIONS STABILITY OF GOLD NANOPARTICLES STABILIZED BY POLYETHYLENE GLYCOL (PEG 0.01%)

Microemulsion template	*ZP*[b] mV
ETAC/Brij30/$HAuCl_4$	30
C6/Brij30/$HAuCl_4$	35
C7/Brij30/$HAuCl_4$	51
i-C8/Brij30/$HAuCl_4$	49
C9/Brij30/$HAuCl_4$	32

All the samples were prepared in the same conditions, at room temperature. After mixing the components (surfactant, organic phase and aqueous phase), the samples were stirred for 45 minutes and let to rest for other 45 minutes. All initial microemulsions were colourless, while after irradiation the samples become coloured, the colour ranging from dark pink to red as an indicator of the AuNPs formation, with specific sizes. In order to obtain solid nanoparticles, microemulsion was "broken" with acetone, followed by centrifugation for 10 minutes at 15000 rot/min and then washed 5 times alternatively with acetone and ethanol to remove the oil and the surfactant. Finally, solid nanoparticles were simply dispersed in ultrapure water.

Instrumental techniques

UV-Vis spectra and DLS measurements (size and Zeta potential) were used for analysing system evolution at nanoscale. UV-Vis measurements were performed using a Jasco V570 spectrophotometer. Dynamic Light Scattering (DLS) measurements were made using Malvern Nanosizer equipment.

Morpho-structural characterization of AuNPs was performed using transmission electron microscopy (TEM) Philips EM 410 and for acquisition and performance measurement, dedicated video camera and analysis software were used. For the preparation of particles specimen, a drop of colloidal solution was drop-cast on a carbon-coated copper grid and dried under ambient conditions. The particle size distribution was analysed by measuring more than 100 nanoparticles based on TEM micrographs.

Results and discussions

The AuNPs prepared by using microemulsion as template and UV light as source for metallic cations reduction, in the same conditions, and by varying the organic phase or gold precursor concentration, have been analyzed by UV-Vis and DLS spectra.

Microemulsion templates for Au(III) photoreduction

The UV photo-induced reduction of Gold(III) in a series of water-in-oil microemulsion produced homogeneous spherical particles with various diameters ranging between 2.5 to 30 nm, depending on the oil type used. They show a good polydispersity (tables 1 and 2). The smallest AuNPs (2.5 nm diameter) have been obtained using Ethyl Acetate (ETAC) as oil, which has a short carbon chain and possesses a polar head by carboxyl group. These features make it less hydrophobic compared to other hydrocarbons used in this study. Thus, its solubilization capacity of surfactant is lower and results into enhancement of repulsive forces between the surfactant hydrocarbon chains, therefore the water droplets size is getting smaller. The largest AuNPs size obtained in i-C8/Brij30/$HAuCl_4$ microemulsion template is due to the branched hydrocarbon chain structure of *i*-C8 that prevents such compact packaging of surfactant chains at the interface water/oil which results in a larger diameter of water droplets.

Zeta potential measurements were used as a stability indicator for aqueous dispersions of AuNPs obtained after their separation from microemulsion templates. If all AuNPs species present in suspension have high, either negative or positive Zeta potential values (outside the range -30 ÷ +30 mV), they tend to repel each other and to avoid aggregation. Therefore, Zeta potential values presented in table 1 suggest a tendency to aggregation of AuNPs into aqueous media, except those prepared using C7/Brij30/HAuCl4 microemulsion system as template. By using this system the AuNPs almost keep their size both in microemulsion and aqueous dispersion.

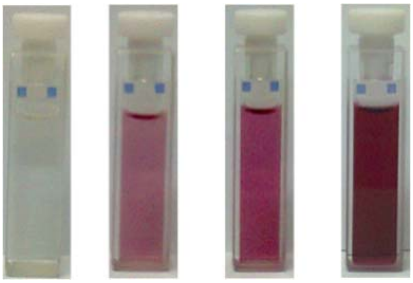

Fig.1. AuNPs dispersed in microemulsion at various irradiation times

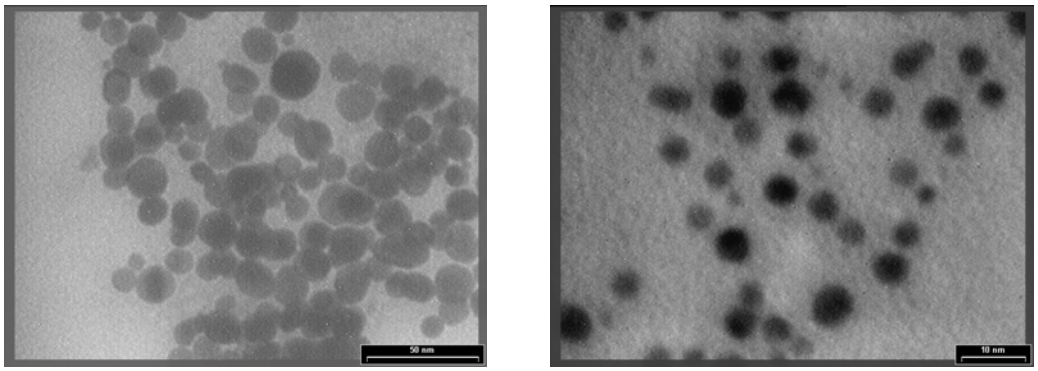

Fig. 2. TEM images of AuNPs photoreduced using C7/Brij30/$HAuCl_4$ (left side) and ETAC/Brij30/$HAuCl_4$ (right side) microemulsion templates, at 1 g/L initial concentration of Au(III) precursor

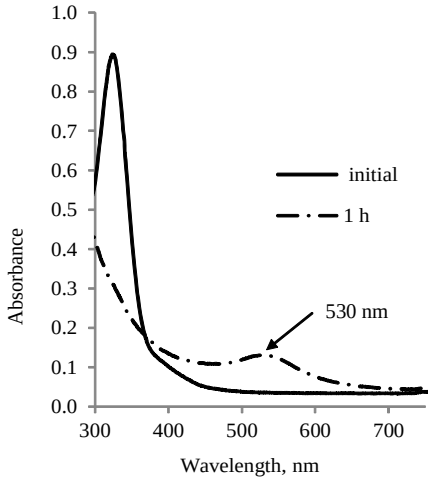

Fig. 3. UV spectra for AuNPs photoreduced using C7/Brij30/$HAuCl_4$ microemulsion template, at 1 g/L initial concentration of Au(III) precursor

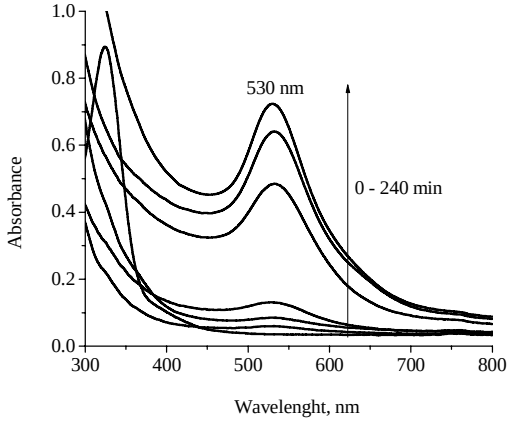

Fig. 4. Evolution in time of AuNPs size and number using UV-Viselectronic spectra

Gold surface modification via polyethylene glycol (PEG)

The optimum microemulsion template is an important requirement for the nanoparticles preparation point of view. As the AuNPs prepared in this work, using different microemulsion templates, do not seem to be very stable in aqueous dispersion, the addition of polyethylene glycol (PEG) stabilizer has been tested (table 3). PEG has been dissolved in water (0.01%) before AuNPs dispersion, and then the sample was stirred for 10 min before measurements.

One can observed that very stable AuNPs of different sizes can be obtained using stabilizer PEG (table 3). A significant improvement in the stability of aqueous dispersion of AuNPs, synthesized in ETAC/Brij30/$HAuCl_4$ microemulsion template, can be noticed, from an unstable sample (ZP = 15 mV) to the almost stable one (ZP = 30 mV).

Gold nanoparticles size depending on the concentration of precursor

The results of this section provide information about the evolution of nanoparticles size at different irradiation time, for different $HAuCl_4$ concentrations, 1, 5 and 10g/L, using C7/Brij30/$HAuCl_4$ microemulsion template. Thus, a qualitative kinetic study for the photoreduction reaction of Au(III) in microemulsions would be performed.

AuNPs formation is marked by microemulsions staining, compared to baseline, when it is colourless (fig. 1).

The shape and size distribution of the AuNPs were determined by transmission electron microscopy. TEM images show spherical gold nanoparticles with average size about 11 nm and 3 nm for AuNPs synthesized using C7/Brij30/$HAuCl_4$ microemulsion template system (fig. 2 (left side)) and ETAC/Brij30/HAuCl4 (fig. 2(right side)), respectively.

The obtaining of AuNPs was also confirmed by UV-Vis measurements (figs. 3 and 4.). The particles exhibited one narrow absorbance band at 530 nm in the UV-Vis spectra which is attributed to the surface plasmon resonance (SPR) band of monodisperse and well-separated gold nanoparticles (fig. 3).

The time evolution of electronic spectra suggests a systematic increase of the peak from 530 nm during the irradiation (fig. 4).

The small broadening of the SPR band, at 5g/L and 10g/L concentrations of $HAuCl_4$, can be related to the coexistence of AuNPs with about 10 and 45, respectively 75 nm sizes (fig. 5).

Based on DLS measurements (fig. 6) one can see that colloidal aggregates are maintaining their initial shape and size (about 10 nm) even after irradiation, thus suggesting that AuNPs take their geometrical characteristics. The larger aggregates presence (40÷100nm) during irradiation, at 5g/L

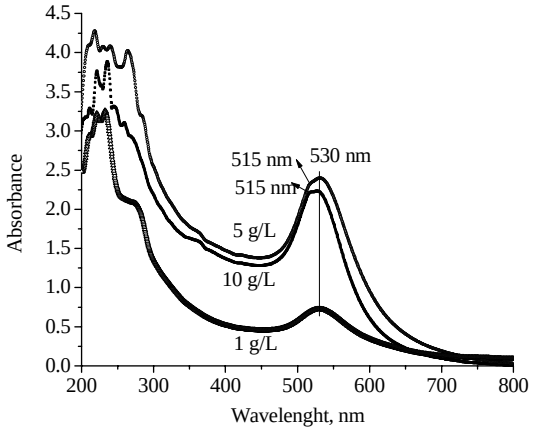

Fig. 5. Electronic spectra of AuNPs templated by C7/Brij30/$HAuCl_4$ microemulsion at 240 min irradiation time and various Au(III) precursor initial concentrations: 1, 5 and 10 g/L

and 10g/L concentrations of $HAuCl_4$, is attributed to bigger AuNPs formation. At higher gold precursor concentration, the number of nanoparticles increases with irradiation time, so the nanodroplets are swollen that lead to their breaking and formation of larger micelles, which become the new template for AuNPs synthesis. In case of AuNPs obtained when C_{HAuCl4}=5 and 10g/L, the second peak, at larger diameters, 45 and 75 nm, has become more intense during irradiation, while the initial one (about 10 nm) losses significantly its intensity after 240 min of irradiation.

Conclusions

A series of water-in-oil microemulsion systems, with the variation of organic phase ETAC/Brij30/$HAuCl_4$, C6/Brij30/$HAuCl_4$, C7/Brij30/$HAuCl_4$, *i*-C8/Brij30/$HAuCl_4$, C9/Brij30/$HAuCl_4$, have been tested for obtaining AuNPs with various sizes. The most stable of these is C7/Brij30/$HAuCl_4$ microemulsion system as template since the AuNPs almost keep their size both in microemulsion and aqueous dispersion.

Very stable AuNPs of different sizes can be obtained using PEG as stabilizer, with a significant improvement in the stability of aqueous dispersion of particles synthesized in ETAC/Brij30/$HAuCl_4$ microemulsion template.

Based on DLS and UV-Vis spectral measurements it was proven that AuNPs maintain the initial shape and the size of microemulsion template is about 10 nm, which suggests that they got their geometrical characteristics. By increasing the irradiation time, longer than 120 min, at higher Au(III) precursor concentrations, 5 and 10 g/L, larger nanoparticles of 45 and 75 nm sizes could be obtained. The corresponding spectral peaks for these latter sizes have become more intense by continuing the irradiation, while the initial one (peak corresponding to about 10 nm) losses significantly its intensity after 240 min of irradiation.

On the whole, this novel technique combines micro-emulsion as one of soft-nanotechnology techniques of wet chemistry with photo-physics of UV-radiation into a unique versatile method to design and obtain controlled nanostructures for multifunctional materials.

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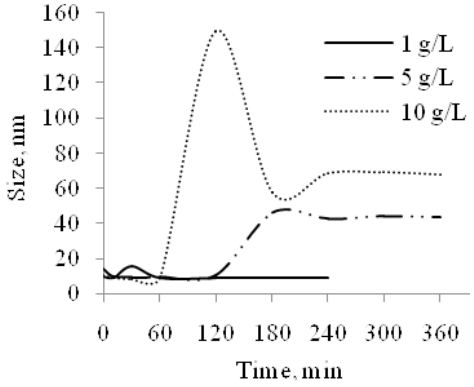

Fig. 6. AuNPs templated byC7/Brij30/$HAuCl_4$ microemulsion at 240 min irradiation time and various Au(III) precursor initial concentrations

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