# A NOVEL STRATEGY FOR THE ALIGNMENT OF SILVER NANOPARTICLES

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**ABSTRACT**
Non-aqueous microemulsions of the ternary system AOT (surfactant), isooctane and ethylene glycol may be composed of spherical or cylindrical aggregates at specific proportions. Using this type of microemulsions it is possible to synthesize silver nanoparticles using silver nitrate as source of the metallic ions.Ethylene glycol serves at the same time as solvent for the silver nitrate and reducing agent of silver ions.The silver nanoparticles synthesized in the spherical aggregates are discrete (average particle size of 10 nm) and do not align. On the other hand, the nanoparticles obtained in cylindrical structures (birefringent phases) align forming linear and ordered arrays. The microemulsions were characterized with optical microscopy between crossed polarizers whereas discrete and linear arrays of silver nanoparticles were observed under transmission electron microscopy to determine their shape and size; HRTEM was used to confirm the crystal structure of the silver nanoparticles and EDS was used for their chemical analysis.

**Keywords**: silver nanoparticles, non-aqueous microemulsions, patterned materials, linear arrays.

## UNA NUEVA ESTRATEGIA PARA LA ALINEACIÓN DE NANOPARTÍCULAS DE PLATA

**RESUMEN**
Las microemulsiones no acuosas del sistema ternario formado por el surfactante AOT, el solvente no polar isooctano y el solvente polar etilenglicol tienen estructuras microscópicas compuestas ya sea de agregados esféricos o cilíndricos.Usando este tipo de microemulsiones es posible sintetizar nanopartículas de plata, usando nitrato de plata como fuente de iones metálicos; el etilenglicol sirve como solvente del nitrato de plata y al mismo tiempo es el agente reductor de los iones de plata. Si las microemulsiones no muestran birrefringencia las nanopartículas sintetizadas se distribuyen homogéneamente (sin alinearse) en la muestra y tienen tamaños promedio del orden de 10nm. En cambio, si la síntesis se realiza en las fases de estructura cilíndrica, se obtienen arreglos de nanopartículas lineales y ordenados con longitudes micrométricas. Las microemulsiones fueron caracterizadas por microscopía óptica entre polarizadores cruzados mientras las nanopartículas de plata, tanto dispersas como alineadas, fueron observadas usando microscopía electrónica de transmisión para determinar su forma y tamaño.Microscopía Electrónica de alta resolución fue usada para confirmar la estructura cristalina de las nanopartículas de plata y la espectroscopía EDS para el análisis químico.

**Palabras claves**: nanopartículas de plata, microemulsiones no acuosas, patrones de materiales, arreglos lineales.

## INTRODUCTION

Metal nanoparticles aligned or organized in varied arrangements are new versions of nanomaterials with important applications in science and technology. Arrangements or alignments of metal nanoparticles can be obtained by different methods; for instance, electrodeposition [1], magnetic alignment [2], or substrate modification [3].

The metal nanoparticles synthesized by chemical methods under different experimental conditions may align to form characteristic linear and ordered arrays when deposited on a grid and observed by transmission electron microscopy. This organization of metal nanoparticles can produce arrays with long-range order in one, two or three dimensions. The formation of these arrangements or alignments of metal nanoparticles has

important implications for the potential applications of these nanomaterials in fields as diverse as electronics, photonics, biological diagnostics, fabrication of chemical sensors, etc.

The results reported in this scientific article, show that it is possible to obtain linear arrangements of silver nanoparticles "in situ" by changing the experimental conditions for the synthesis of the particles in AOT-isooctane-ethylene glycol microemulsions. The described method involves the synthesis of the silver nanoparticles in a non-aqueous microemulsion; the continuous phase is isooctane and the dispersed phase is ethylene glycol (which also serves as solvent and reducing agent of the metal precursor). The surfactant dioctylsulfosuccinate (AOT) is the stabilizer of the microemulsion. The source of silver ions is silver nitrate, which is dissolved in ethylene glycol. The results show that under specific experimental conditions for the chemical synthesis, the obtained nanoparticles align in highly ordered arrays. These arrays consist of parallel lines of silver nanoparticles with lengths in the micrometer scale.

## MATERIALS AND METHODS

All reagents were of 99% purity and purchased from Sigma-Aldrich. They were used as received. The reagents are sodium dioctyl sodium sulfosuccinate (AOT), isooctane, ethylene glycol and silver nitrate.

The non-aqueous microemulsions were prepared in 12 ml clear glass tubes with screw caps. First, AOT was added to isooctane and dissolved; then ethylene glycol was added to the mixture, and the sample was stirred for 30 minutes. The microemulsions were sealed with parafilm and allowed to stand at room temperature (25 $^{0}$C) for a week. The prepared microemulsion concentrations correspond to two points in the phase diagram: one that enables the alignment of the nanoparticles (isooctane rich region) and another that does not generate alignment of the nanoparticles (area rich in ethylene glycol). The compositions employed are shown in Table 1.

**Table 1.** Composition of the microemulsions employed in the synthesis of silver nanoparticles. The sample S1 yielded aligned nanoparticles; with sample S2 no alignment was observed. The composition is given in mol %.

| Sample | AOT | Isc | EG |
|---|---|---|---|
| S1 | 9.3 | 84.1 | 6.6 |
| S2 | 5.5 | 2.4 | 92.1 |

For the synthesis of the silver nanoparticles, a 20mM silver nitrate solution was added to the already prepared microemulsion and stirred with a vortex vigorously for 30 minutes. The samples were left to stand for one week at room temperature. During this period the samples changed color indicating the presence of nanoparticles, which were characterized by transmission electron microscopy (TEM), energy dispersive X-ray (EDS) and polarized light microscopy. For the TEM and EDS analysis a 10 µl sample was deposited on a carbon-coated copper grid (400 mesh) with a formvar film. Then the grid was introduced into a vacuum chamber for 3 days prior to observation under the electron microscope. The electron microscope used was a JEOL 2010F TEM operating at 200 kV. X-ray energy-dispersive (EDS) spectra were detected at 1000 counts/s, with a total acquisition time of 300 s, with the Energy Dispersive X-ray spectrometer QUANTAX 200-TEM (Bruker, Germany). For the polarized light optical microscopy experiments, 500µl of the microemulsion sample were placed onto a borosilicate glass microscope slide and allowed to dry at room temperature before observation. The optical microscope used was an Olympus model IX 71.

## RESULTS AND DISCUSSION

In the microemulsion method [4], metallic ions are chemically reduced in the polar domains of

microemulsions, allowing the growth of metallic nanoparticles. We have combined this procedure with the polyol method for the nucleation of silver nanoparticles. Our approach has been successful since silver nanoparticles have been produced in practically all the regions of the microemulsion phase diagram. Nevertheless, the characteristics of the nanoparticle population are different, depending on the relative concentrations of the components of the microemulsion. For instance, the synthesis in the ethylene glycol rich regions produces bigger nanoparticles than the synthesis in the isooctane rich regions. This is due to the fact that in the first situation, the concentration of reducing agent (ethylene glycol) is higher.

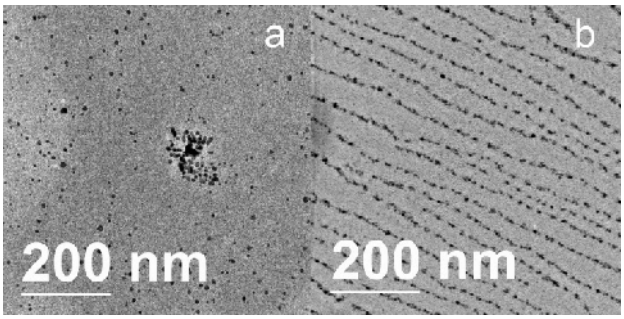


**Fig. 1**. Representative TEM micrographs of the obtained silver nanoparticles. a) Particles synthesized in a microemulsion with spherical aggregates. b) Particles prepared in a microemulsion with cylindrical micelles.

Even if we observe a majority of quasi-spherical particles, the nanoparticle population is polydisperse in size and shape. In most of the cases, the nanoparticles appear scattered over the entire TEM observation field. They are not aligned neither ordered in regular patterns, as shown in figure 1a. This is due to the fact that the nanoparticles are synthesized in isolated polar domains: the spherical micelles of the microemulsion.

However, the particles can be aligned if they are synthesized in cylindrical micelles. For this, we have studied a region of the microemulsion phase diagram where the aggregates are cylindrical. The idea is that the particles will remain confined in the cylindrical domains when deposited in the TEM grid. Figure 2 shows a polarized optical microscopy image of the dried microemulsion composed of cylindrical aggregates. The conical pattern is characteristic of a hexagonal phase, i.e., of an array of parallel cylindrical aggregates.

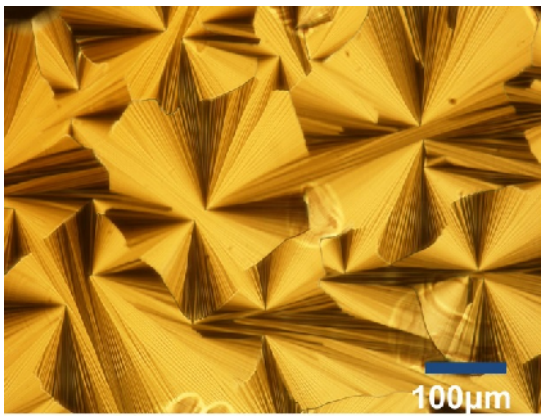


**Fig. 2.** Polarized light optical microscopy image of the microemulsion sample composed of cylindrical aggregates. The texture is typical of a hexagonal phase.

The result of the synthesis in this sample is shown in figure 1b. In this micrograph, we appreciate well-defined stripes of spherical particles. The lines are more or less parallel and are as long as one micron. In each stripe, the silver nanoparticles are confined in a gap of 20 nm. The periodicity of the array is of the order of 70 nm. The average linear nanoparticle density is 60 particles per micron. The nanoparticles have an average diameter of 7 nm. The particles are relatively monodisperse; in fact, the polydispersity index, defined as the ratio of the diameter standard deviation to the average diameter is 0.13, a value consistent with monodisperse particles. Note that the obtained nanoparticle arrays span areas of some square microns and are reproducible. In the literature, there are reports of more or less similar arrays obtained by other methods [5 – 8].

We have confirmed that the particles are silver nanoparticles. In figure 3 we display a high-resolution TEM micrograph of one particle. The interplanar distances measured from the picture agree with those of an fcc silver nanocrystal. This result is confirmed by the

interplanar distances measured from a simulated diffraction pattern obtained by a fast-Fourier transformation procedure (FTT plot not shown).

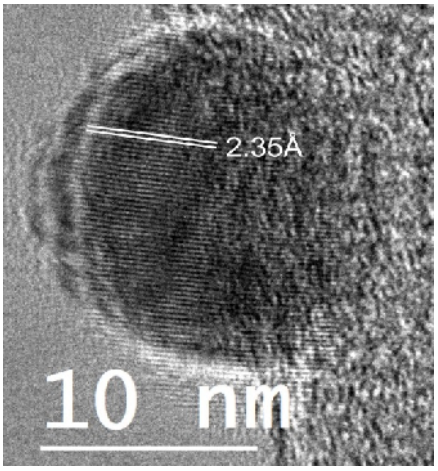


**Fig. 3.** High-resolution TEM micrograph of a silver nanoparticle. The measured interplanar distances correspond to an fcc silver crystal.

In addition, the Energy Dispersive Spectroscopy (EDS) analysis reveals that the particles are composed of silver (see figure 4). The presence of sodium, sulfur and oxygen is due to remaining surfactant molecules that surround the nanoparticles (the AOT formula is $C_{20}H_{37}NaO_7S$).

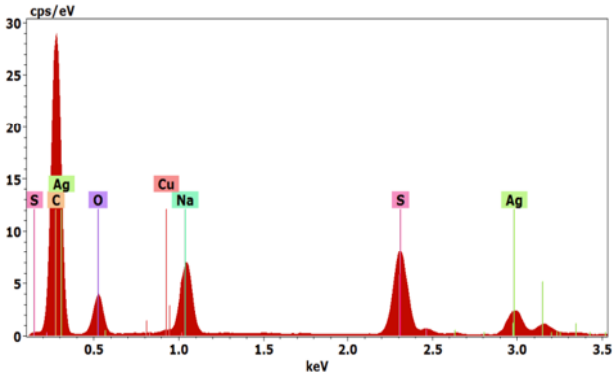


**Fig. 4.** EDS spectra of a silver nanoparticle.

## CONCLUSIONS

In this paper we have briefly reported on a novel strategy for the alignment of silver nanoparticles. In our approach, the particles are synthesized by the polyol method in the cylindrical micelles of a microemulsion. When the sample is allowed to dry on a TEM grid, the particles remain aligned along parallel stripes as long as one micron. The obtained patterns can be useful in applications such as photonics. Several scientific questions remain open; for instance, how the polydispersity in the nanoparticle population can be controlled with this method; other interesting question is related to the possible effect on the synthesis of the use of other surfactants. These questions will be addressed in forthcoming works.

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