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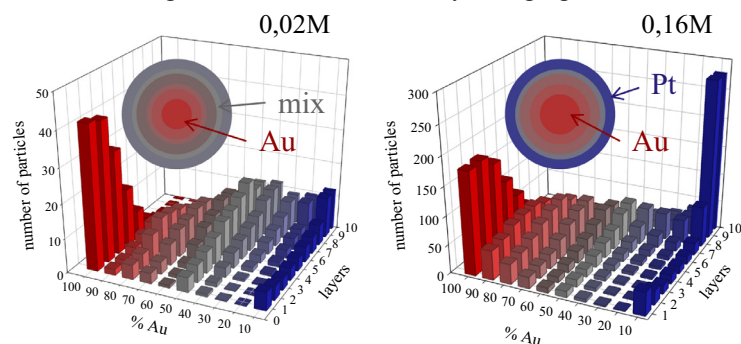
Regular Article

# Bimetallic nanoparticles synthesized in microemulsions: A computer simulation study on relationship between kinetics and metal segregation

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## GRAPHICAL ABSTRACT

Metal arrangement can be modified by changing concentration



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## ABSTRACT

Computer simulations were carried out to study the origin of the different metal segregation showed by bimetallic nanoparticles synthesized in microemulsions. Our hypothesis is that the kinetics of nanoparticle formation in microemulsions has to be considered on terms of two potentially limiting factors, chemical reaction itself and the rate of reactants exchange between micelles. From the kinetic study it is deduced that chemical reduction in microemulsions is a pseudo first-order process, but not from the beginning. At the initial stage of the synthesis, redistribution of reactants between micelles is controlled by the intermicellar exchange rate, meanwhile the core and middle layers are being built. This exchange control has a different impact depending on the reduction rate of the particular metal in relation to the intermicellar exchange rate. For the case of Au/Pt nanoparticles, the kinetic constant of Au (fast reduction) is strongly dependent on intermicellar exchange rate and reactant concentration. On the contrary, the kinetic constant of Pt (slower reduction) remains constant. Therefore, the fact that the reaction takes place in a microemulsion affects more or less depending on the reduction rate of the metals. As a consequence, the final nanostructure not only depends on difference between the reduction rates of both metals, but also on the reduction rate of each metal in relation to the intermicellar exchange rate.

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## 1. Introduction

Microemulsions as reaction media has been a fascinating field of research for the last few decades, mainly due to microemulsion

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droplets can be used as templates to synthesize nanoparticles [1]. From the first reported synthesis of metal particles via microemulsions by Boutonnet et al. [2], different kind of materials have been successfully prepared via microemulsions, including metals [3–7], oxides [4,8], semiconductors [9], silica [10], polymers [11,12], superconductors [13], bimetallic nanoparticles [14,15] or even subnanometric clusters [16]. The principal reason for using microemulsions in the preparation of nanoparticles is the efficient control of size, shape and composition of resulting nanoparticles thanks to confinement of reactants inside micelles and particle stabilization by surfactant [2,16–18]. The small size in these materials confers new properties and open up possibilities of novel applications, both in basic research and in different industrial fields [19–21], such as catalysts, drug delivery or high density magnetic recording.

The influence of number variables (reagent concentration, surfactant, solvent, aqueous phase content, cosurfactant) on the final nanoparticles synthesized in microemulsion has been reported. However, in spite of the great deal of progress made in the last years in understanding reactions in microemulsions, the interaction between the dynamic behaviour of the microemulsions and the kinetics of nanoparticle formation is still far from clear. “By microemulsion dynamics, we mean the fact that the domains are not static ones, but are in continuous movement and collision with each other” [22]. The dynamic behaviour of microemulsions depends on its composition, temperature, concentration and nature of reactants [23]. The synthesis of nanoparticles inside the micelles occurs according to a mechanism involving coalescence of micelles, exchange of reactants between micelles and nucleation of particles inside a micelle. At first, reverse micelles have been depicted as nano-reactors whose main function was template the growing nuclei into nano-sized particles. Since then, however, a rather richer and dynamical role of reverse micelles was also suggested [24,25]. Further mechanisms, such as autocatalysis and ripening, have been also assumed [25]. An autocatalytic growth takes place when larger particles grow faster due to increased surface area. The Ostwald ripening occurs when larger particles grow as smaller ones disappear, due to the dissolution of small particles and their re-deposition on the surface of larger ones, which leads to a further growth of the large particles at the expense of smaller ones. All these processes require the exchange of material between micelles, so the easy with which channels communicating colliding droplets can be opened, and the rate of diffusion of reactants between droplets play a relevant role in nanoparticle formation. The effects of microemulsion dynamics on the kinetics of nanoparticle synthesis have not been taken into account in a methodical way, and it is considered a key variable affecting the nanoparticle formation in microemulsions. Our hypothesis is that the synthesis of nanoparticles in microemulsions has to be considered in terms of two potentially limiting factors, chemical reaction itself and the rate of reactants exchange between micelles.

As part of our ongoing effort to improve understanding of the synthesis of nanoparticles in microemulsions as reaction media [26–29], we have focused here on the synthesis of bimetallic nanoparticles. Bimetallic nanoparticles present new properties different from monometallic counterparts [30,31]. The presence of a second metal redefines the interatomic interactions, which results in changes in surface and structure of bimetallic nanoparticle. Designing the metal distribution, composition and size of bimetallic nanoparticles would be crucial for various applications. As a case in point, the goal of industrial catalysis is to attain the largest catalytic activity, connected to high selectivity and durability against deactivation [30]. With this purpose, noble bimetallic nanocatalysts have been synthesized by different strategies, as summarized in various reviews [32–34]. It was proved that bimetallic nanocatalysts show noticeably enhanced catalytic

performance compared to their parent single metal nanoparticles [30,35,36].

Apart from the inherent chemical and physical properties of the constitutive metals, the catalytic activity relies notably on the metal distribution in the nanostructure [31]. The two metals can be fully mixed, in a core-shell arrangement, with a surface enriched in one metal, and/or a metal enrichment in the inner part, that is, with a different degree of metal segregation. The control of the metal distribution in bimetallic nanoparticle is crucial to the enhancement of catalysts performance [37–40]. For example, different Au-Pt nanoarrangements are been used as catalyst depending on the particular reaction: the best distribution for electro-oxidation of methanol is a Pt-Au alloyed shell [41], but a Au-core/Pt-shell distribution is preferred to catalyze oxygen reduction reaction [42,43] and formic acid electro-oxidation [44]. One of the most common procedures to control the size and composition of bimetallic nanoparticles is the simultaneous reduction of the two metals via microemulsions [45–47]. As far as the current state-of-the-art is concerned, it is complicated to predict the results of experiments designed to produce novel nanostructures via microemulsions, not only due to the inherent complexity of the reaction media, but also due to the difference in reduction rates of the two metals. In fact, many results come from trial-and-error experimentation. A strong tool for elucidating the interplay between chemical reduction itself and microemulsion dynamics is computer simulation. With the aim of evaluating whether microemulsion dynamics affects equally to both metals, in view of their different reduction rates, in this contribution we focus on a kinetic study of bimetallic nanoparticle formation in microemulsions by the one-pot method and its impact on final nanostructure.

## 2. Materials and methods: Simulation model

A simulation model has been developed to predict the metal distribution of bimetallic nanoparticles obtained via the microemulsion route [28].

### 2.1. Kinetic course of the reaction

A microemulsion is described as a set of 15,000 micelles, which carry the metal salts (e.g.  $[\text{AuCl}_4]^-$  and  $[\text{PtCl}_6]^{2-}$ ) and the reducing agent (e.g. hydrazine) (5000 micelles containing each kind of reactant). Concentration inside micelles can be modified by varying the initial average number of reactants, which are distributed among the micelles according to a Poisson distribution:  $\langle c[\text{AuCl}_4]^- \rangle = \langle c[\text{PtCl}_6]^{2-} \rangle = 2, 16, 32,$  and  $64$  metal ions in a droplet, which corresponds, respectively, to  $0.01 \text{ M}, 0.08 \text{ M}, 0.16 \text{ M}$  and  $0.40 \text{ M}$ . Once each kind of reactant is located inside a set of micelles, the microemulsions are mixed.

Micelles move and collide with each other. The diffusion of micelles is assumed to be governed by Brownian motion. In the previous algorithm developed to simulate the synthesis of simple nanoparticles (non bimetallic), micelles are all randomly placed in a 3D box and performed random walks to nearest neighbour sites by choosing at random the direction of the motion at each step [27,48]. This random walk was subject to the exclusion principle (the trial movements resulting in micelles overlapping are excluded) and periodic boundary conditions were applied at the ends of the lattice. Two micelles collided when they occupied contiguous lattice sites. To save computation time, the model was improved by choosing the two colliding micelles at random. In doing so, the material content of each micelle is stored but not its position. Both ways of simulating the motion and collision lead to exactly the same results [49]. The second method was used to

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