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Monolayer kinetic model of formation of gold nanoparticles by reducing agents hexadecylaniline or bovine serum albumin

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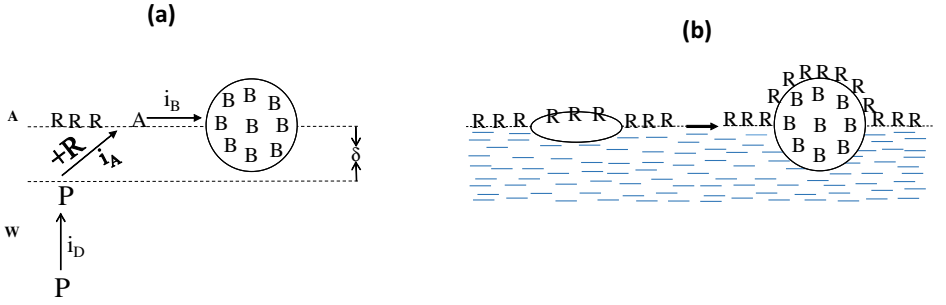
HIGHLIGHTS

- Synthesis of gold NPs at A/W interface of HDA or BSA monolayers was performed.
- Au^0NPs growth kinetics was followed by measuring of $\Delta A(t)_\pi$ at barostatic condition.
- A corresponding kinetic model of NPs formation was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

In the formation of metal nanoparticles (NPs) in aqueous solution two distinguishable processes take place: the nucleation and the NPs' growth. In the present paper is proposed an experimental approach which aims to clarify whether the interfacial organization of the reduction reaction plays a role during the growth process. The gold nanoparticles were formed in hexadecylaniline (HDA) or bovine serum albumin (BSA) monolayers spread on aqueous chloroauric acid solution. The kinetics of the NPs formation was followed by measuring of the monolayer properties, namely the change of the surface area with time at constant surface pressure, $\Delta A(t)_\pi$, as well as the NPs' size and shape by AFM after Langmuir-Blodgett (LB) transfer. The proposed simple monolayer system has few advantage for better control of the physicochemical parameters of the reduction reaction which occurs at the air/water interface, e.g. the surface concentration and the interfacial organization of both components- tetrachloroauric acid ($HAuCl_4$) and HDA (or BSA), the degree of unfolding of BSA molecules, the number of reaction sites involved in interactions etc.

A kinetic model of the interfacial reaction of NPs' formation at the air/water interface was developed and the kinetic constants of the reduction reaction (k_r), of nuclei formation (k_1), and NPs' growth (k_2) were estimated. It was found that the rate constant of the reduction reaction is many order of magnitude higher than the rate constant of NPs' formation. The formation of critical nuclei and their subsequent growth under the action of the reducing agent HDA were found to be 100 times faster in comparison with the action of BSA as a reductant.

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1. Introduction

In the last two decades the nucleation and the growth of metal nanoparticles (NPs) in aqueous solutions have been intensively investigated [1–3]. Various experimental methods (e.g., UV–vis, dynamic light scattering (DLS), X-ray spectroscopy, etc. [4,5]), were employed for monitoring the processes of NPs' formation as well as for describing the kinetic mechanisms of the NPs' growth. The mechanisms of NPs' formation in solution were considered by numerous convenient theoretical approaches [2,6]. Among the many proposed in the literature, now firmly established and mostly applicable is the Finke-Watzky (F-W) mechanism [7,8]. It has two steps, the first one is a slow continuous nucleation ($A \rightarrow B$), which is followed by fast autocatalytic NPs' growth ($A + B \rightarrow 2B$). Applying F-W model for the formation of gold nanoparticles (Au^0NPs) by Turkevich synthesis (reduction of chlorauric acid $HAuCl_4$ by sodium citrate), Georgiev et al. [9,10] have measured the intensity of plasmon maximum by means of UV-vis, together with visualization by AFM of the Au^0NPs' growth in the course of their synthesis and have determined the kinetic constants of the corresponding processes in the F-W model. Their results also showed that AFM might be useful both for the characterization of the obtained NPs as well as a kinetic tool.

The bovine serum albumin (BSA) coated NPs were considered to be one of the best vehicles for drug release and also for numerous biomedical applications. Recently, BSA conjugated Au^0NPs were synthesized for testing their applicability as drug delivery vehicles in systemic circulation [11]. This study have shown some of the important physicochemical aspects required for an appropriate synthesis of BSA-conjugated NPs in which the unfolded BSA is an essential reaction component.

For tuning and control of the optical, electronic and catalytic properties which are tightly related to the size and shape of the Au^0NPs, a better understanding of the mechanisms of their formation seems indispensable. When some amphiphilic molecules organized in Langmuir-Blodgett (LB) monolayers at the air/water (A/W) interface are used for the entrapment of metal nanoparticles then the environment in which the nanoparticles grow is controlled both by physical confinement and chemical capping [12]. Usually, the incorporation of metal ions within the molecules of the Langmuir monolayers occurs at the A/W interface closely to the polar part of amphiphilic molecules [13]. It was reported by Swami et al., that the presence of strong oxidizing agent (e.g. silver or gold ions) in the subphase caused the oxidation of the headgroup of the amphiphile (i.e. reduction of the ions in the subphase) and thus led to the formation of nanoparticles [14] or nanoribbons [15] under the Langmuir monolayer. Lately, the involvement of the advanced X-ray methods for studying the formation of Au^0NPs in Langmuir monolayers and Langmuir-Blodgett (LB) films were also reported. The in situ grazing-incidence X-ray diffraction (GID) was successfully applied for simultaneously probing the octadecanethiol monolayer structure and the surface of the gold particle [16]. S. Kundu et al., obtained X-ray reflectivity data from octadecylamine LB-films, transferred in the course of the nanoparticle formation within the monolayer environment [17].

Despite numerous publications for the use of Langmuir monolayers as "reductant templates" for the nanoparticles' synthesis at A/W interface, the mechanisms of nucleation and NPs' growth remain somehow unexplored. In particular, it would be interesting to clarify whether the interfacial organization of the reduction reaction plays a role during the growth process.

In the present paper we propose an experimental approach for studying kinetics of the interfacial synthesis of Au^0NPs by adopting and modifying the F-W kinetic model. The NPs were formed either in 4-hexadecylaniline (HDA) or in Bovine serum albumin (BSA) monolayers spread on aqueous $HAuCl_4$ solution. The appearance of gold nuclei and their growth were followed by measuring the monolayer properties, namely the change of the surface area in time at constant surface pressure (π), i.e. $\Delta A(t)_\pi$, as well as measuring Au^0NPs' size and shape by AFM after LB-transfer. The proposed simple monolayer system has few advantages. At first, it offers a better control of the physicochemical aspects of the reduction reaction, organized at the A/W interface, surface concentration and interfacial organization of both components- $HAuCl_4$ and HDA (or BSA), the degree of unfolding of BSA and the number of sites involved in the interaction, etc. Secondly, there is a clear distinction between the two consecutive phases of nucleation and growth. At last but not least, the monolayer system gives unique possibility to synthesizing metal NPs by using insoluble reducing agents, such as HDA, BSA or any other appropriate for this purpose amphiphilic compound.

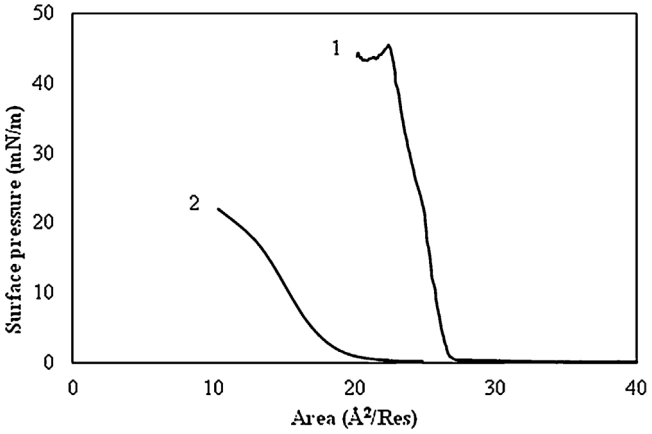

Fig. 1. Isotherms surface pressure (π) versus mean area (A) per molecule for HDA (*curve 1*) and per amino acid residue for BSA (*curve 2*) monolayers.

2. Materials

Analytical grade tetrachloroauric acid ($HAuCl_4 \cdot 3H_2O$) was purchased from Panreac (PanreacQunmica S.A.U., Spain). Bovine serum albumin (BSA) was purchased from Sigma–Aldrich (Germany) in form of lyophilized powder. The molecular mass of BSA was about 69 kDa. Also from Sigma - Aldrich (Germany) was ordered, 4-Hexadecylaniline (HDA) with molecular weight 317.55 and purity 97%. In all experiments was used pure water from Milli-Q system (Millipore Corporation, Boston, USA).

3. Methods and experimental results

Two kinds of experiments for measuring of the surface area (ΔA) as a function of time (t) were performed: (i) at constant surface pressure $\pi = 5mN/m$, with HDA as reducing agent and (ii) with BSA as reducing agent at $\pi = 10mN/m$. Those values of the constant surface pressures were chosen because they correspond to the states of the monolayers of closely packed HDA or BSA molecules at the A/W interface, and were determined from $\pi(A)$-isotherms shown at Fig. 1. Commercial surface balance (KSV 2000, Finland) equipped with platinum plate and a "zero-order" trough [18] was used for measuring the change of surface area $\Delta A(t)$ at constant surface pressure π. The trough contained a reaction compartment with volume 50 cm^3 and surface area $A_0 = 50cm^2$, and a reservoir compartment with surface area 280 cm^2. The two compartments communicated with each other through two narrow surface channels, each 0.5 cm wide [19]. The subphase in both compartments was pure water. The HDA monolayer was spread at the A/W interface from chloroform solution by Hamilton micro syringe.