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Radiation induced synthesis of silver nanoshells formed onto organic micelles

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Abstract. Synthesis of metal nanoshells around organic micelles is achieved through radiolysis of aqueous solutions of surfactant self-assembled in spherical micelles and metal ions. The formation of the metal nanoshells is evidenced by UV-visible spectroscopy and Small Angle X-ray Scattering.

PACS. 81.07.-b Nanoscale materials and structures: fabrication and characterization – 61.10.Eq X-ray scattering (including small-angle scattering) – 82.50.Kx Processes caused by X-rays or gamma-rays – 82.70.Uv Surfactants, micellar solutions, vesicles, lamellae, amphiphilic systems, (hydrophilic and hydrophobic interactions)

1 Introduction

Metallic nano-objects are of great interest in the field of nanoscience. Their robust and functionalizable structure combined with interesting physical properties make them ideal structures for fundamental research and applications. Metallic nanoshells appear as a typical system to observe physical properties induced by limited size. Their optical properties have been studied in the case of silica beads covered with gold or silver (40−250 nm radius) [1,2]. Although these nano-shells present interesting properties, varying the nano-object geometry rapidly appears as a new challenge. Structures as nano-cups and nano-caps have been obtained by using a chemical strategy associating metal coverage deposition and partial passivation of the substrate sites [3]. However, methods based on the deposition of metal atoms onto a solid substrate are not easily modified for obtaining new geometries. In order to develop a more versatile process to produce nano-objects, we develop a strategy based on the association of the self assembled properties of amphiphilic molecules and the radiolysis synthesis process. Indeed, the variety of structures formed by amphiphilic molecules leads to a large panel for potential templates [4]. On the other hand, the radiolysis procedure leads to monodisperse metal aggregates [5] from which one can expect to obtain homogeneous metallic layers. We have already demonstrated the potentiality of carboxylic groups as templates. Indeed, we succeeded in forming a thickness controlled silver layer anchored to a behenic acid Langmuir monolayer [6]. In this paper, we present an extension of this process to the 3D case. Irradiating an aqueous solution containing silver ions and spherical linoleate micelles leads to the formation of silver nanoshells onto the organic micelles. Silver and linoleic acid have been chosen since silver reduction properties [5] and linoleic acid micelles have been extensively studied [7]. Moreover, silver choice is also leaded by the huge activity field in colloids and surfaces due to their application in catalysis and in photochemistry process.

2 Experimental section

Silver sulfate (Sigma), absolute ethanol (Prolabo) and linoleic acid (Merck) are pure grade reagents. Linoleic acid ($CH_3(CH_2)_4CH = CHCH_2CH = CH(CH_2)_7COOH$) is an amphiphilic molecule which spontaneously aggregates into spherical micelles in basic aqueous solutions. Its critical micellar concentration (cmc) is measured at 2 $\mathrm{mmol\,L^{-1}}$ for pH = 10.5 [7]. Linoleic acid (LH) was

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stored under argon atmosphere. Because of its slow spontaneous autoxidation, only freshly made solutions were used. LH (3 $\mathrm{mmol\,L^{-1}}$) was dissolved in ultrapure water (Millipore system, 18 MΩ cm), then the pH was adjusted to 10.5 with sodium hydroxide in order to deprotonate quantitatively the carboxylic groups and to form spherical sodium linoleate micelles. Silver sulfate Ag_2SO_4 (10 $\mathrm{mmol\,L^{-1}}$ in Ag^+) was dissolved in the alkaline solutions only after the formation of stable linoleate micelles to avoid the formation of silver hydroxide. This addition was performed in a dark room due to silver photosensitivity. The ratio $R = [\mathrm{LH}]/[\mathrm{Ag^+}] = 0.3$ was chosen for having at least several Ag^+ ions per LH head-group. It is limited by the formation of AgOH precipitate. Absolute ethanol CH_3CH_2OH (0.2 $\mathrm{mol\,L^{-1}}$) as an $HO^\bullet$ radical scavenger [8] was added to the solutions. The solutions were degassed by bubbling with argon prior to irradiations.

γ–irradiation was provided from a ^{60}Co source (LCP, Orsay University) at the dose rate 4 $\mathrm{kGy\,h^{-1}}$. The solutions were irradiated under argon atmosphere at 25 °C. γ–irradiation of deoxygenated water leads to the formation of three radical moieties $HO^\bullet$, $H^\bullet$ and hydrated electrons e^-_{aq}. Their radiolytic yields of formation G are 0.29 $\mu\mathrm{mol\,J^{-1}}$ for $HO^\bullet$, 0.28 $\mu\mathrm{mol\,J^{-1}}$ for e^-_{aq}, and 0.06 $\mu\mathrm{mol\,J^{-1}}$ for $H^\bullet$ [9]. In aqueous solutions containing 0.2 $\mathrm{mol\,L^{-1}}$ in absolute ethanol, $HO^\bullet$ and $H^\bullet$ radical species are readily scavenged by alcohol molecules [8] leading to secondary radicals $CH_3^\bullet CHOH$ ($R^\bullet$) with:

$$G_{\mathrm{R}^\bullet} = G_{\mathrm{HO}^\bullet} + G_{\mathrm{H}^\bullet} = 0.35\ \mu\mathrm{mol\,J^{-1}}. \tag{1}$$

Note that $HO^\bullet$ could react with linoleate in a well-known chain propagation reaction leading to dienic hydroperoxide products which strongly absorb at 234 nm [7]. However, after irradiation, no absorption increase at this wavelength is observed, meaning that radio-induced peroxidation of linoleate does not occur since ethanol concentration is much more higher than that of linoleate molecules. Hydrated electrons e^-_{aq} and secondary radicals $R^\bullet$ are strong reductive agents. They homogeneously reduce silver ions into atoms which coalesce and finally form silver aggregates [10]:

$$\mathrm{Ag^+} + e^-_{aq}\ \ (\text{or}\ \ \mathrm{R^\bullet}) \rightarrow \mathrm{Ag^\bullet}\ \ \text{reduction} \tag{2}$$

$$n\mathrm{Ag^\bullet} \rightarrow \mathrm{Ag}_n\ \ \text{coalescence.} \tag{3}$$

These metal particles are synthesized with a homogeneous distribution and a maximal reduction yield

$$G_{red.max} = G_{e^-_{aq}} + G_{\mathrm{R}^\bullet} = 0.63\ \mu\mathrm{mol\,J^{-1}}. \tag{4}$$

For the ratio $R = [\mathrm{LH}]/[\mathrm{Ag^+}] = 0.3$, a part of the reducing radical species (e^-_{aq} and $R^\bullet$) may react with linoleate micelles lowering the reduction yield of silver. It is then essential to determine, in our experimental conditions, the effective radiolytic yield of silver reduction in order to know the dose needed for total reduction of the silver ions. For this purpose, solutions of silver linoleate have been irradiated with increasing doses. The study of the dependence of silver aggregates absorption spectra as a function of the irradiation dose allowed us to determine this effective radiolytic yield: $G_{\mathrm{red}} = 0.6\ \mu\mathrm{mol\,J^{-1}}$ in our experimental conditions. This yield is close to $G_{red.max}$ which shows that only a small fraction of reducing radical species reacts with linoleate micelles. Then, the total reduction of Ag^+ occurs at doses higher than

$$D(\mathrm{Gy}) = \frac{[\mathrm{Ag^+}](\mathrm{mol\,L^{-1}})}{G_{red}(\mathrm{mol\,J^{-1}})} = 16.67\ \mathrm{kGy}. \tag{5}$$

The aqueous solutions of silver aggregates were characterized by spectrophotometric measurements by means of a Beckman DU 70 spectrophotometer using quartz cells with an optical pathway of 0.2 cm. Characterization by Small Angle X-ray Scattering experiments were performed at the BM2-D2AM CRG beamline at the European Synchrotron Radiation Facilities (ESRF — Grenoble) which experimental setup is described in reference [11]. The photon energy was 16 keV ($\lambda = 0.0777$ nm). We use the same cylindrical glass capillary for all solutions in order to maintain constant the scattered signal by the capillary. This is mandatory for further subtraction with such low scattering system. All the measured spectra are centro-symetric. Thus standard procedures described elsewhere [12] were used to convert measured intensities to differential scattering cross-sections (σ).

3 Results and discussion

Silver particles (several nanometers in diameter) are characterized by an intense plasmon absorption band around 400 nm, due to a collective oscillation of the electron gas [5]. In order to probe whether the radio-induced aggregation process occurs in the presence of linoleate micelles, the spectra obtained after irradiation of the studied solution have been recorded. The spectrum obtained for the total reduction of silver ions (20 kGy) presents a strong absorption band at 400 nm, in agreement with the formation of silver aggregates (inset of Fig. 1). The study of the dependence of the absorption spectra as a function of the irradiation dose allowed us to determine the extinction coefficient $\epsilon_\lambda = 12\,000\ \mathrm{L\,mol^{-1}\,cm^{-1}}$ which is close to the classical values corresponding to silver nanoparticles [13]. One can observe in the spectrum a small absorption band around 235 nm which is already present prior to irradiation. It is due to the small amount of dienic hydroperoxide products formed by autoxydation of linoleate molecules.

In order to probe whether the silver objects formed by radiolysis are classical colloids or nanoshells, we have used a form sensitive technique such as Small Angle X-ray Scattering (SAXS). Figure 1 shows the SAXS spectrum of the studied solution before and after irradiation with a dose of 20 kGy (the spectra are subtracted from the pure water scattering). Before irradiation, the spectrum exhibits weak oscillations at high Q values. After irradiation, the curve exhibits more pronounced oscillations and at smaller Q values. This suggests that the objects initially present in the solution become denser and bigger. This is in agreement with the formation around

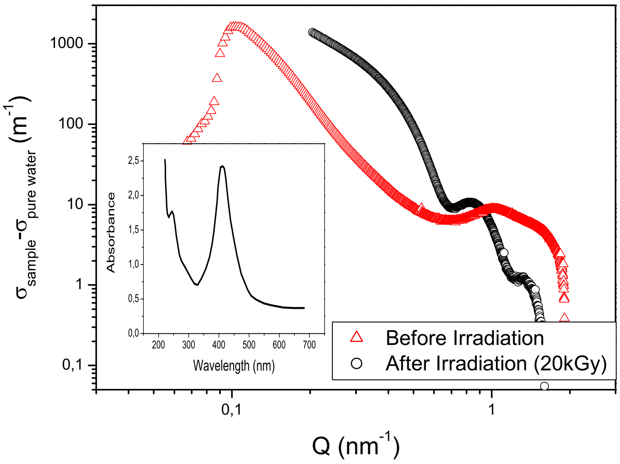

Fig. 1. SAXS spectra obtained on a linoleate solution (3 mmol L^{-1}) with 10 mmol L^{-1} of Ag^{+} ions and 0.2 mol L^{-1} of CH_3CH_2OH at pH = 10.5. The triangle are for the non irradiated solution, and the circle are for the irradiated solution with a dose of 20 kGy. Inset: UV-visible absorption spectrum of the irradiated solution at 20 kGy. Dilution 1/10. Optical length: 0.2 cm.

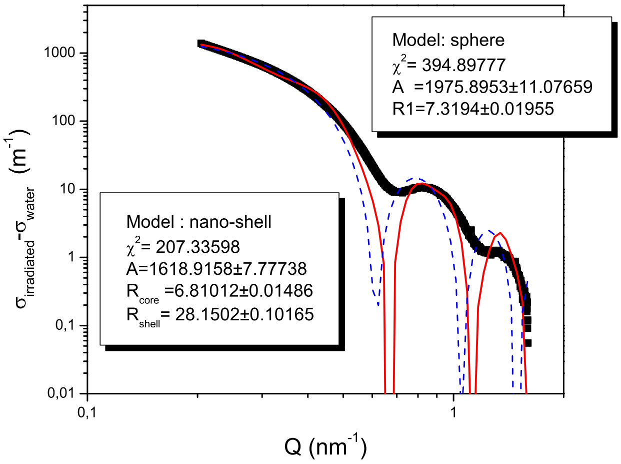

Fig. 2. SAXS spectra of a 20 kGy irradiated linoleate solution (3 mmol L^{-1}) with 10 mmol L^{-1} of Ag^{+} ions. The lines are fitted curves using two different model, the sphere (dashed line) and the shell (continuous line).

the organic micelles (small size — weak contrast with X-ray) of nanoshells (bigger size — higher contrast to X-ray) but also with the formation of cylindrical colloids. After irradiation, the experimental data were adjusted using two different models. In Figure 2, the data are fitted using the model of a sphere [14] (dashed line). Such a model is not able to fit both the oscillation period and the intensity decrease. Thus the scattering objects are not plain spheres. A fit with a model of a nanoshell (obtained by subtracting the scattering of a plain sphere of radius R_{core} to a sphere of radius R_{shell} [14]) is also presented. The calculated curve describes rather correctly the evolution of the scattering cross section either the oscillation and the decrease of the intensity. Only two features are not described. The depth of the minima is not correctly reproduced. This could be due to the polydispersity of the objects which could decrease the depth of the minima [14]. The minima could also be smoothed by resolution effects. The second feature is the last oscillation which is not entirely described. This could be due to the various subtractions which are rather dependent on the transmission measurement. However this effect is observed for large Q values where the difference between the curves is weak. The obtained core radius of the formed nanoshells, 6.8 nm, is in agreement with what is expected for rather long chain amphiphilic surfactant. The shell thickness $R_{shell} - R_{core} = 21.3$ nm is rather large and suggests according to the initial ratio between linoleate head-group and silver ions that not all the micelles lead to the formation of a nanoshell but explains the UV-visible absorption spectroscopy result.

As a conclusion, these experiments give strong evidences of the formation of silver nanoshells using radiolysis reduction of metal ions onto linoleate micelles. This demonstrates that the electrostatic interaction between the anionic head-group of linoleate surfactant and cationic silver ions is sufficiently strong to induce the coalescence of the reduced silver atoms around the micellar organic templates.

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