Quantitative analysis of structure, size and strain distributions of Au nanoparticles

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Introduction

The determination of structural and morphological parameters in nanoparticles (NPs) of few nanometers is generally a difficult task and still requires the development of new methods of analysis [1-6]. Noble metal NPs, such as Au and Ag, are particularly complex since size reduction effects leads to structural transition from fcc bulk-like structure, i.e. cuboctahedron (> 4 nm in diameter), to decahedron (2-3 nm) and icosahedron (<1.5 nm). Besides that, synthesis conditions may lead to metastable structures and usually more than one type of structure is presented in the sample [4]. Here, we have studied structural aspects of Au NPs capped with alkanethiols of different lengths (hexa-C6, dodecane-C12 and hexadecane-C16). To extract information about the influence of the capping layer on the structure types, size and strain distributions, synchrotron XRD data were analyzed by the method proposed by A. Cervellino et al. [5] together with Extended X Ray Absorption Fine Structure (EXAFS) and Small Angle X Ray Scattering (SAXS).

Methods and Materials

Au NPs were synthesized following the Brust method [1,2]. Briefly, $HAuCl_4$ was reduced by $NaBH_4$ in a two-phase system (water-toluene) in the presence of alkanethiols. Three samples were synthesized by varing the alkanethiol length (C6, C12 and C16). The samples were named Au-C6, Au-C12 and Au-C16. SAXS experiments were performed in diluted solutions at SAXS beamline, LNLS, Brazil (λ=1.755Å). EXAFS experiments at Au L_3-edge and low temperature (20K) were performed at XAFS beamline, LNLS, Brazil. XRD patterns were obtained in powder samples at XPD beamline, LNLS, Brazil in θ-2θ geometry and λ=1.45864 Å. The XRD data were analysed by a Rietveld-like approach, where the domain size distribution, strain-size dependence and structure type concentrations were refined [5]. Four model structures were considered: cuboctahedron (CUBO), icosahedron (ICO), decahedron (DECA) and blunt decahedron (BDEC). The BDEC structure was obtained from DECA by removing the equatorial belt of atoms. An amorphous contribution was also included in the present analysis, as discussed below.

Results

SAXS measurements showed that the three samples present close size distributions, with average size of about 2 nm. EXAFS analysis showed that the Au-Au near neighbors inter-atomic distance (NND) is slighly contract compared to bulk Au (~1%) and similar for the three samples. This contraction is much smaller than the one expected for free clusters, due to the Au-S interaction on particle´s surface [2]. On the other hand, XRD analysis pointed out important differences related to structural distributions among samples. While the major population in the Au-C6 sample is the ICO, for Au-C12 sample is the BDECA and for the AuC16 sample is the CUBO (Table 1). An amorphous contribution were found for the three samples and the strain profles were similar. The average domain sizes obtained by XRD are systematically smaller than the NP size derived by SAXS.

Discussion

SAXS results showed that the alkanethiol length did not significantly affect the average size of Au NPs. EXAFS results suggested that the Au-S interaction was similar for all samples. However, the XRD analysis showed that the alkanethiol length may have affected the particle growth and the atomic arrangement. In this size range, the DECA is the energetically favored structure in free clusters but the results showed that all samples present a structure distribution with different predominant population. It is also important to remark that the high quality XRD data used in this work allowed us to improve the methodology previously proposed [5] by including the BDECA to the family of structure types. This led to a general improvement of the best-fit solution and a residual scattering corresponding to a distance distribution function with only a peak at 3 Å, very close to the NND in Au, that can be attributed to the residual scattering of point defects at the surface, like ad-atoms.

TABLE 1: Mass fraction (%) & GoF (godness of fit) values derived frorn the XRD analysis.

Sample	CUBO	ICO	DECA	BDECA	GoF
Au-C6	16.39	60.37	11.55	11.68	1.706
Au-C12	0.27	37	0	62.74	1.944
Au-C16	40.44	16.77	20.63	22.16	4.109

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