Journal of Electron Spectroscopy and Related Phenomena 184 (2011) 375–378

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

Functionalized nanoparticles in aqueous surroundings probed by X-ray photoelectron spectroscopy

Johan Söderström[a,*], Niklas Ottosson[a], Wandared Pokapanich[a], Gunnar Öhrwall[b], Olle Björneholm[a]

[a] Department of Physics and Astronomy, Uppsala University, Box 516, 751 20 Uppsala, Sweden
[b] Max-lab, Lund University, Box 118, 221 00 Lund, Sweden

ARTICLE INFO

Article history:
Received 7 December 2010
Received in revised form 15 February 2011
Accepted 21 February 2011
Available online 30 March 2011

Keywords:
Nanoparticle
Soft X-ray
Photoelectron spectroscopy
Liquid colloid
Liquid micro-jet

ABSTRACT

In this paper we present the first core-level photoelectron spectroscopic study of solid nanoparticles in liquid water. The particles are SiO_2-based with an average diameter of 70 nm and functionalized with carboxylic groups. Despite that the sample is very dilute, we show that it is possible to obtain reasonable photoemission signal containing chemical information about both the ligands and the outermost parts of the SiO_2-based core of the nanoparticles. We argue that this is due to a significant enrichment of the dispersed particles at the liquid/vapor interface. This proof-of-principle study expands the field of X-ray photoelectron spectroscopy by adding a new, wide and important class of systems that can be studied.

1. Introduction

Nanoparticles (NPs) exhibit size-dependent properties that differ significantly from those observed for larger particles or the infinite solid of the same constituent material, which often is related to the increased surface-to-volume ratio with decreasing size. If a particle is sufficiently small, the curvature can strain the bonding of surface atoms/molecules and thereby dramatically alter the particle's surface reactivity – a property that can be tailored and exploited for efficient catalytic reactions [1]. Many current, and possibly also future, chemical applications employ NPs in contact with a liquid medium, see e.g. Refs. [2,3]. Due to their useful properties, NPs are today used in large-scale industrial applications and are thus gradually becoming more frequent in our surroundings, even though their potential toxicity and impact on natural ecosystems are not well understood at present [4,5]. It is therefore of both practical and fundamental interest to increase our molecular-scale understanding of the complex and important NP containing liquid systems.

X-ray photoelectron spectroscopy (XPS) is a powerful tool for investigations of free atoms, molecules and solid samples. The method provides a local probe of the sample's electronic structure with elemental and site-specificity and is thus, in principle, ideally suited for fundamental characterization of NPs. In recent years XPS has proven to be useful in the study of free clusters [6] (and references therein) and free NPs [7,8], it should be noted that the technique to generate free NPs employed in Ref. [7] might leave the NP surrounded by a large number of water molecules – this is not specified in the paper but our understanding is that this might be the case.

However, no one has yet demonstrated the applicability of XPS to NPs dispersed in liquid media. In addition to overcoming the experimental challenges associated with performing XPS on volatile liquids – something which was only recently overcome with the development of the liquid micro-jet technique [9,10] – dispersed NPs present new challenges given the low fraction of NPs dispersed in a liquid system. Firstly, this means that the samples are typically very dilute, presenting a sensitivity challenge. Secondly, the NPs may easily precipitate or agglomerate in the nozzle of the liquid micro-jet, thus presenting sample handling challenges. As the NPs are orders of magnitude larger than atomic or small molecular ions fewer agglomeration steps are needed in order to block the nozzle of the liquid jet. Initial tries indicates that the blocking of the nozzle strongly depends on the ligands, most likely the risk of blocking the nozzle also depends on the concentration and size of the NPs.

In this paper we present the first results from NPs dispersed in liquid studied with soft X-ray photoelectron spectroscopy. The aim of the paper is not to perform a complete characterization of the quite complex ligand-covered and dye-doped NPs dispersed in liquid water. It is instead to demonstrate that XPS indeed can be used to probe the electronic structure of NPs in an aqueous medium,

* Corresponding author. Tel.: +46 18 471 36 05.
E-mail address: Johan.Soderstrom@fysik.uu.se (J. Söderström).

0368-2048/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.elspec.2011.02.006

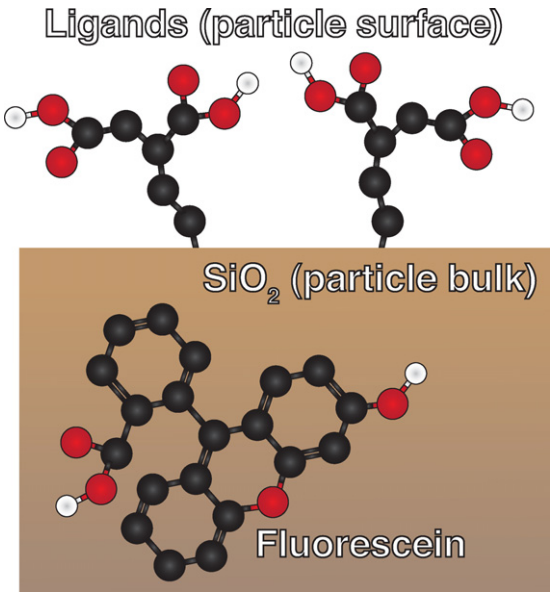

Fig. 1. The general structure of the NPs. The bulk of the NPs consists of SiO_2 with silylated fluorescein dye molecules covalently bound to the SiO_2 bulk. For simplicity we label the "bulk" of the NP as the entire volume occupied by SiO_2 (and the dye). The particles are covered with organic ligands, which we label the particle surface, which creates a clear distinction between the "bulk" and surface.

giving rise to separated signals from the ligands, the ligand–particle interface and from the outermost parts of the particle "bulk". The present study thus expands the domain of XPS to include studies of a new and large class of important systems. To simplify the discussion in this paper we have defined the "bulk" of the NPs as the SiO_2 core of the NPs (which also contains silylated fluorescein, discussed in detail later) and the surface of the NPs as the carbon-based ligands. A cartoon of a NP with the ligands is presented in Fig. 1 where the interface between the SiO_2-based "bulk" of the NP is depicted together with the organic ligands constituting the surface of the NP, in the bulk the fluorescent dye is also schematically shown.

2. Experimental

The experiment was performed at the I411 beamline at MAX-lab, Lund, Sweden [11,12]. The liquid micro-jet setup used to produce the beam of NPs in water suspension has been presented elsewhere, see Ref. [13]. The interested reader is referred to a recent and comprehensive review on the liquid micro-jet technique [14] and references therein.

The linearly polarized synchrotron light impinges on the liquid sample in an interaction chamber where a differentially pumped Scienta R4000 photoelectron spectrometer is mounted at an angle of 54.7° (the "magic angle") relative to the polarization plane [15]. The photoelectron spectrometer was used with 200 eV pass energy and a curved entrance slit of 0.5 mm, giving a broadening of ~0.25 eV. The exit slit used for the monochromator was 100 μm, giving a photon bandwidth of ~0.56 eV at 360 eV and ~0.16 eV at 150 eV, which are the two photon energies used in these measurements – this corresponds to a total resolution of ~0.6 and ~0.3 eV, respectively.

The binding energy scale has been calibrated against valence band spectra of liquid and gas phase water, recorded in parallel with the presented core-level measurements, and aligning the $1b_1$ state of liquid water to 11.16 eV [16]. During the experiments we observed a slight charging of the liquid jet due to variations in the photon flux, which decreases over time due to the decreasing current in the MAX II storage ring. This introduces an additional

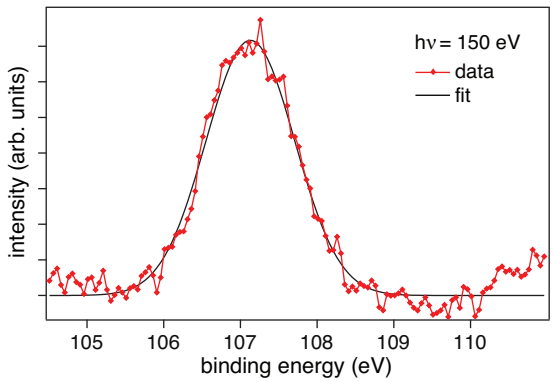

Fig. 2. The Si2*p* region of the investigated functionalized SiO_2-based NPs recorded with a photon energy of 150 eV. In this figure a linear background has been removed. No attempts of resolving the spin-orbit components has been made. The spectrum shows that it is possible to record spectra from the "bulk" of the NPs with reasonable statistics.

broadening of less than 0.13 eV in addition to the experimental contributions discussed above. This broadening is not Gaussian in shape, but it is small compared to the other broadenings, therefore allowing for satisfactory fits of the data using Gaussian line shapes.

The commercially available NPs were obtained from micromod [17], prod. no. 42-02-701, which are spherical monodisperse SiO_2-based NPs with a diameter of 70 nm and a polydispersity index of less than 0.2. In the SiO_2 "bulk" a fluorescent dye (silylated fluorescein) is covalently bonded to the silica throughout the whole particle volume. Furthermore, the particles are functionalized with carboxylic groups attached to alkyl chains covering most of the surface, see Fig. 1. These NPs are quite complex, and their exact composition is in fact not known to us. Having carbon-chain ligands and a SiO_2 core with silylated fluorescein, these NPs however provide us with a number of chemically inequivalent sites, situated at different radial regions. They are thus well suited for our main purpose, namely to demonstrate that XPS indeed can be used to probe the local electronic structure of NPs in aqueous surroundings with sufficient chemical sensitivity to separate contributions from the ligands, the ligand–particle interface and the particle "bulk".

The NPs were suspended in de-ionized H_2O where 50 mM NaCl were further added in order to minimize the charging effects due to photoionization. The particle concentration was $\sim 9\times10^{12}$ particles per ml which equals ~15 nM of NPs. Since each NP contains on the order of 5×10^6 Si atoms, the corresponding total concentration of Si atoms is on the order of 70 mM which defines a theoretical upper limit of the amount of silicon atoms that can contribute to the Si2*p* signal. It is possible to estimate the concentration of Si atoms that can give rise to the XPS signal the following way. For a particle this size most of the atoms will not give rise to the XPS signal due the IMFP discussed below. A reasonable estimate is that only 1% of the Si atoms are close enough to the surface to contribute to the signal. In Ref. [7] the authors have estimated that the observed signal comes from ~1/6 of the NP surface (electrons emitted from other parts of the surface cannot make it to the spectrometer due to a "shadowing" effect by the NP itself). By employing the same assumption here, and considering that only 1% of the Si atoms can give rise to the signal the concentration of "relevant" Si atoms is on the order of 100 μM.

3. Results and discussion

In Figs. 2 and 3 we show Si2*p* and C1*s* core photoelectron signals originating from the functionalized SiO_2-based NPs i.e. from both the SiO_2 "bulk" and the organic ligands (the surface). We thus demonstrate that the sensitivity challenge discussed above is sur-