



Metal nanoparticle size distribution in hybrid organic/inorganic films determined by high resolution X-ray photoelectron spectroscopy



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ABSTRACT

We report on the application of high resolution X-ray photoelectron spectroscopy (HR-XPS) to provide a fast identification of the size distribution of metal nanoparticles (NPs) embedded in a polymer matrix. An accurate spectral analysis was performed on the metal photoelectron core level to determine the specific calibration curve which relates the metal NP core level binding energy shift to its size, which was independently measured by transmission electron microscopy. We have fully characterized the binding energy shifts in the case of silver NPs on a polythiophene based polymer layer. This work shows how this procedure can be applied to characterize multimodal size distributions of metal NPs on a statistical adequate sample area, without having typical experimental limitations of a TEM experiment. Moreover, this technique can give access to chemical analysis and by alternating ion beam sputtering and XPS analysis, the NP diffusion along the growth direction can be revealed.

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1. Introduction

Hybrid materials composed of metal nanoparticles (NPs) dispersed on or into a polymer or an organic matrix are nowadays widely used for enhancing the organic layer mechanical, electrical and optical properties [1]. In this framework, growing efforts are devoted to the improvement of hybrid optoelectronic devices such as sensors [2], organic solar cells [3], OLEDs [4], and also promising low cost non-volatile organic memory devices [5,6]. More specifically, in many technologically relevant applications, the control over the NPs size distribution, density and tridimensional distribution inside the organic (semi)-conducting layer is a basic requirement to be able to control the material and the device properties.

The synthesis of hybrid layers composed of metal NPs distributed on (or into) a polymer matrix is usually carried out following two main methodologies. The first one is by using chemically synthesized NPs dispersed in a colloidal solution. This approach allows having NPs characterized by a very narrow size distribution, but the depositing on a polymer matrix is poorly controlled because NPs can undergo aggregation during the drying process. This makes this methodology not suited for specific applications where a homogeneous spacial distribution of NPs is required [7]. On the other hand, physical deposition techniques

such as thermal or e-beam evaporation of metals, allow obtaining a homogeneous NPs distribution, thanks to the random nucleation of metal islands, but the size distribution is known to be wider and poorly controlled. The cohesive interaction between the metal atoms is generally sufficient to overcome their adhesion to the organic substrate material, so that isolated cluster islands are spontaneously formed by diffusion on the polymer surface following a Volmer–Weber growth mode. The clustering process is affected by many parameters such as the atomic diffusion, the metal–polymer interaction, the evaporation rate, and the surface roughness [8]. Transmission electron microscopy (TEM) is one of the preferred techniques for evaluating the size distribution of evaporated NPs. Meanwhile, there are many constraints associated with this technique; first of all, the material has to be deposited on TEM compatible supports (grids); then, the hybrid film thickness is limited to few hundreds of nanometers; and finally, information on the particle distribution in the out of plane direction is not easily accessible, except by performing time-consuming tomographic analysis. Moreover, when recording TEM images at high magnification, as it is needed for the detection of particles with few nanometers size, one has generally to extract statistics from the size distribution on a fairly small sample area.

In this contribution, we want to illustrate how with high resolution X-ray photoelectron spectroscopy (HR-XPS) it is possible to characterize the size distribution of NPs deposited on or even into a polymer layer. As we will illustrate, the size identification is performed by exploiting the so-called *size effects*, which occurs in nanometer-sized metal clusters. The main size effect is the core

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level binding energy (BE) shift which is proportional to the cluster size. Core levels BE shifts have been reported for a multitude of free or supported metal clusters, the metals include gold [9–12], palladium [13], samarium [14], platinum [15], silver [16–18], titanium [19], copper [20], iron [7], cesium [21], etc.

The origin of BE shifts in metal clusters is well described in the literature, especially for small, non-supported clusters. For those very small clusters, the BE shifts are well explained in terms of initial and final state effects [22,23]. The initial state effects in small non-supported clusters become relevant when the number of surface atoms, with a lower coordination number, becomes comparable to bulk atoms. In the present work we deal with few nanometers sized clusters deposited on a semi insulating substrate; in this case the main initial state effect is related to the specific interaction between the cluster and the surrounding matrix [24,25]. The evidence of a charge transfer from the metal NPs to the polythiophene matrix was confirmed by the HR-XPS spectra of the S2p as shown in Fig. 1. The interaction with the Ag NPs is evident from the extra peak, appearing at lower BE. The main final state effect which contributes to the BE shifts in our experiment, is related to the coulomb interaction between the positive charge left on the whole cluster surface during the photoemission process, and the leaving photoelectron [26].

Regarding the small amplitude of the size effect on the metal NP core level peak position, it is almost needless to stress that one has to control very efficiently any charging effect during the XPS experiment. In this work, we have investigated four hybrid samples composed of silver NPs grown by thermal evaporation on a thiophene based polymer layer. The plasma polymerized thiophene (pp-Th) layer was deposited directly on TEM grids as described in the experimental section. As schematically shown in Fig. 2, different size distributions of silver NPs were obtained starting from an initial size distribution, and then reducing it by exposing it to an argon ion beam for different beam energies and total sputtering time. This original approach resulted in the synthesis of four films with homogeneously distributed Ag particles of few nanometers down to sub-nanometer diameter. The final size distribution in each sample was characterized by TEM. This size distribution was used to interpret the Ag3d HR-XPS spectra, for finally being able to associate the photoelectrons core levels BE shifts to the specific particles size interval.

2. Experimental

In this experiment we studied four hybrid samples composed of Ag NPs of different sizes supported on a polythiophene based

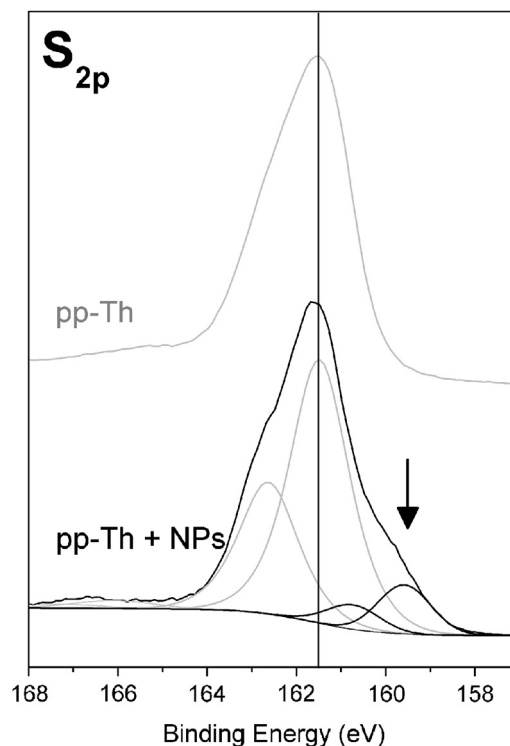


Fig. 1. High resolution S2p XPS spectra from a plasma polymerized thiophene layer as described in the text (top curve), and a pp-Th layer decorated with Ag NPs (bottom curve). The weak low BE doublet (in black) results from the interaction of the thiophene molecules with the silver NPs.

polymer layer. The polythiophene layer was deposited directly on *Formvar*[®] coated Cu grids (300 mesh) by low pressure RF plasma polymerization. The polymerization was achieved by continuously injecting a mixture of thiophene vapor and argon into an inductively coupled plasma discharge. The reactor base pressure was 1 mTorr, the thiophene vapor pressure was set to 100 mTorr and then argon was added to reach the final pressure of 400 mTorr; the RF power was set at 25 W driven in a pulsed mode at 25 Hz frequency and 20% duty cycle. The final polymer thickness was 100 nm, as determined by a stylus profilometer from *Veeco Instruments* (Surface Profile Measuring System, *Dektak*). More details about the polymer deposition are beyond the scope of the present work. Then Ag was thermally evaporated in situ, with a deposition rate, calibrated by a quartz crystal microbalance, of 0.3 Å/s and a

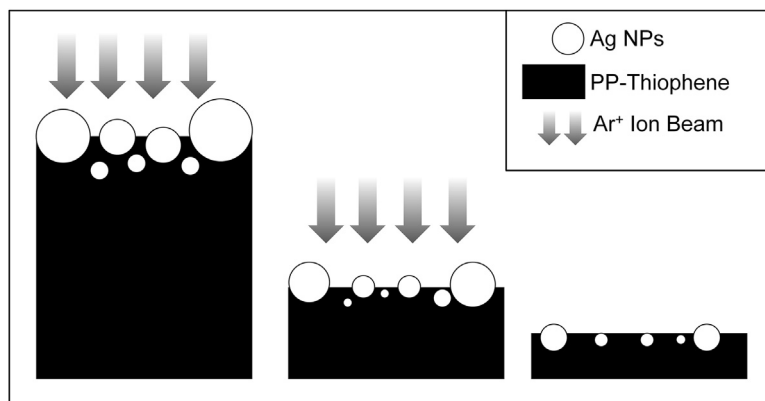


Fig. 2. Schematic description of the experimental strategy. Four different Ar beam sputtering conditions have been applied in order to obtain hybrid layers containing different size distribution of isolated Ag nanoparticles.

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