

Consideration of the Potential of High Energy Resolution X-ray Absorption and X-ray Emission Experiments to Track Changes in Oxidation States on Nanoparticle Materials

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Precise control and characterization of nanomaterials at working conditions are essential for further rational applications in many areas important for modern society. Penetrating properties of X-ray radiation in combination with advanced spectroscopy schemes are an ideal tool to investigate modifications of nanomaterials with extraordinary precision. Here, we present preliminary results on the controlled oxidation of copper nanoparticles and exploration of X-ray absorption spectroscopy to follow electronic and structural changes. The described pilot experiment raises questions on the applicability of high energy resolution X-ray detection schemes in potential future investigations aimed at following reversible reduction/oxidation processes at nanoparticle surfaces.

topics: copper nanoparticles, X-ray absorption spectroscopy, X-ray emission spectroscopy, core-shell structures

1. Introduction

Nanomaterials prepared from earth-abundant and inexpensive metals have attracted considerable attention because of their potential as viable alternatives to rare and expensive noble metals. In this context, copper nanoparticles (NPs) have been studied extensively due to the broad range of potential applications in, e.g., sensing, solar cells, catalysis, photocatalysis, biomedicine, optics, and electronics [1]. Copper has a range of oxidation states (0, I, II, and III) due to the presence of unpaired electrons in their *d*-orbitals, making it very reactive and prone to undergo a variety of reactions. In particular, copper metal nanoparticles exhibit intense light absorption and scattering in the region of the solar spectrum due to the excitation of collective electronic excited states (plasmons) [2]. At visible wavelengths, the interaction of the incident light with conduction band electrons of nanoparticles resonantly excites coherent oscillations of the electron density of states. This phenomenon is called localized surface plasmon resonance (LSPR) and allows the generation of hot electron clouds that can be used as triggers for light-induced energy conversion and storage processes. The plasmonic properties, such as the resonant wavelength and the intensity of LSPR, are governed by the nature, size, and shape of plasmonic metals [3]. Obviously, the bottleneck for Cu NPs application is their stability, as they are

prone to rapid oxidation, particularly at the relevant nanoparticle sizes (< 50 nm). From thermodynamic perspectives, both oxygen molecules and water are able to easily oxidize the surface of copper NPs under ambient conditions. According to recent studies, the oxidation mechanism in nanosized materials is not trivial and involves the formation of a core-shell structure (metal core and oxide shell) and internal voids attributed to the nano Kirkendall effect (NKE) [4]. It was shown that the oxidation process is governed by fast outward diffusion of Cu^+ ions through the oxide layer, which strongly depends on the degree of metal-to-oxide conversion. Many approaches have been tested to increase the stability and prevent the oxidation of copper NPs. Among them, surface modification via additional post-treatment (e.g., with capping ligands, photoreduction, chemical etching) has prevailed as the dominant strategy [5, 6]. Employed as an encapsulation material, a transparent matrix prevents oxidation processes, but changes the optical and electronic structure properties of nanoparticles, which excludes any systematic studies of the material with respect to potential applications.

Despite extensive studies on Cu NPs materials and their properties, a number of unanswered questions remain. In particular, there is a significant knowledge gap concerning the fundamental aspects, e.g., the effect of NPs surface oxide on the localized surface plasmon resonance strength and coupling of

the surface oxide with charge-accepting units, such as semiconductors and molecular linkers. Since the material's electronic structure links the optical absorption, electronic, and chemical properties of the material, the quantitative determination of the density of electronic states of NPs is necessary to correlate the high-efficiency light-absorption yield of NPs with the low efficiency of charge transfer processes.

In the present manuscript, we address materials methodology for plasmon-enhanced solar-driven chemistry, aiming to investigate the influence of copper surface states on the nanoparticles–molecular linker assembly capabilities. In the discussed proposal, we evaluate the exploration of X-ray penetrating capability and elemental sensitivity of the X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES), further supported with high-energy experimental schemes. The combined approach exhibits the potential to map *in situ* the electronic structure around the Fermi level under controlled oxidation/reduction conditions in aqueous solution [5]. This provides the basis to determine Cu–oxide/Cu–metal compositions in the obtained CuOx@Cu core–shell type structures and deconvolute the contributions of bulk and surface states.

2. Experiment

The pilot experiments were performed at the PETRA III synchrotron P65 beamline. In short, X-rays delivered by 11 periods undulator were monochromatized with Si(111) monochromator crystals and sized down to $1000 \times 500 \mu\text{m}$. As a sample, the liquid Cu NPs (25 nm in diameter, purchased from Sigma-Aldrich) solution in distilled water with 1 mM concentration of Cu atoms was used. For the measurements, 30 mL of the sample solution was placed in the flat flow cell with Kapton windows, providing a 1 mm-thick liquid sheet at the X-ray beam spot. The flow was induced by a peristaltic pump connected to the cell through flow tubes. The total fluorescence XAS spectra were recorded by scanning the X-ray energy around the Cu *K*-edge, and the X-ray fluorescence spectra were recorded with a silicon drift detector (SDD). In order to mimic the surface/bulk oxidation change of NPs, a water solution of hydrogen peroxide (H_2O_2) was added in two steps into the liquid sample: first 5 mL of 1 mM, then 0.3 mL of 9.8 M (as-purchased concentration, Sigma Aldrich). Measurements of reference materials, i.e., Cu foil and CuO pellet (1 wt% in cellulose), were conducted in the transmission mode.

The X-ray absorption spectra are sensitive to the local atomic and electronic structures around the absorbing atom and thus can be used to verify the nature of copper species. The normalized copper *K*-edge spectra collected for Cu NPs and reference compounds are presented in Fig. 1. The reference Cu metal foil, CuO reference, bare Cu NPs, and

oxidized Cu NPs are marked by black, blue, red, and green lines, respectively. The measured Cu foil and CuO spectra are equivalent to the spectra reported in the literature [7]. The spectral shape of Cu is dominated by the $1s$ to $4p$ excitation feature at the absorption edge (due to dipole-allowed transitions) and the following resonant structures resulting from the scattering of photoelectrons on surrounding atoms. The reference CuO spectrum is shifted toward higher energies and shows a very weak pre-edge structure at 8977 eV due to the $1s$ to $3d$ excitation and at-edge feature related to an unoccupied $4p$ orbital. The spectrum collected for bare Cu NPs already shows differences with respect to the one for Cu metallic foil. This effect may be explained by a partial oxidation of the NPs surface, as the apparent shift of the XAS data towards higher energy confirms a partial change in the oxidation state. As previously mentioned, the copper nanoparticles quickly oxidize to polycrystalline cuprous oxide (Cu_2O) under ambient conditions. After a controlled addition of an oxidant agent (H_2O_2), a clear change of the spectral features is observed, indicating the change of Cu NPs into the more oxidized form consisting of Cu(I) and Cu(II) species. This result is confirmed when comparing the *in situ* oxidized NPs with reference CuO powder. In order to determine the ratio of surface/bulk oxidation and form of the formed structures, future experiments are needed that will cover different concentrations of oxidants and sizes of metallic NPs. An important element of the research will be to address the possibility of reducing the so-oxidized samples and exploring the controlled *in situ* formation of Cu NPs in a fully metallic state. At this point, the mentioned experiments are beyond the scope of the present manuscript.

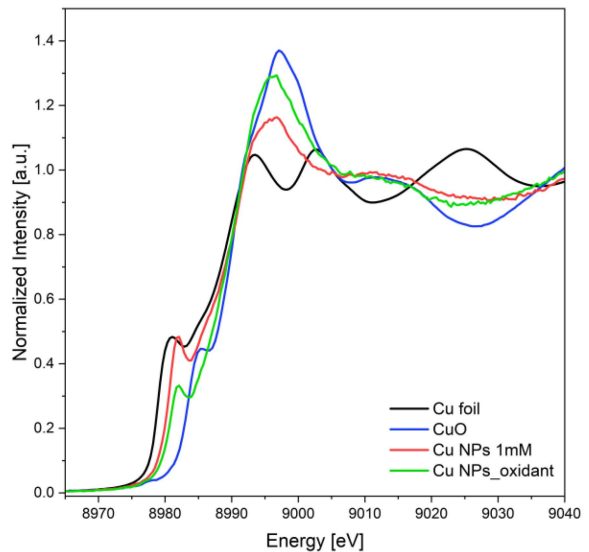


Fig. 1. Normalized copper *K*-edge XAS spectra for Cu foil, bare Cu NPs, Cu NPs after oxidation, and CuO reference.

3. Discussion

The obtained result provides very important information on the eventual feasibility of using X-ray absorption spectroscopy to monitor *in situ* changes in surface oxidation and reduction processes in a controlled manner. First of all, the detected spectral changes are significant and therefore allow for a very precise determination of the surface oxide-to-bulk metal ratio. From the obtained signal differences, we estimated that the detection of oxide-to-bulk contribution can be determined down to a 1% level. However, in order to address and evaluate structural changes caused by oxidation and reduction mechanisms, different NPs sizes should be subjected to future experiments.

An important aspect of *in situ* and *operando* experiments is the consideration of high-resolution Cu *K*-edge XAS experiments in the fluorescence mode instead of typical XAS measurements. The natural lifetime broadening at the *K*-edge of Cu amounts to 1.4 eV and is larger than the Darwin width broadening induced by monochromator crystals, which equals 1.26 eV. Therefore, the application of high energy resolution detection schemes, such as the use of von Hamos or Johann crystal spectrometers, will deliver significant improvement to the experimental resolution. This is of importance, especially for direct *1s* to *3d* excitation in CuO that is visible in XAS spectra as a weak pre-edge structure and is mostly hindered by natural lifetime broadening of the core-hole. For this reason, the detailed analysis of this spectral feature is challenging and often involves dedicated fitting procedures. We should emphasize that the improvement in spectral resolution does not only relate directly to the width values of lifetime broadening and experimental broadening, but also refers to the type of spectral function describing the discussed contributions. This effect is rarely discussed in the literature, but is worth mentioning because the lifetime broadening is determined by the Lorentz distribution, while the experimental contribution is given by the Gaussian function. Due to the fact that the Lorentz function decays as $1/\text{energy}$ and the Gaussian contribution as $1/\text{energy}^2$, the latter is vanishing much faster, making the broadening of spectra features less extended in the energy. As a consequence, even if both widths of broadening are equal, the quality of experimental data convolved with the Gaussian distribution exhibits better resolution than for the Lorentz one. This observation has been confirmed in a range of experiments where the introduction of high energy resolution schemes for detection delivered higher spectral quality even for small differences between core-hole and instrumental contributions [8, 9]. At this point, the discussed effect still should be validated experimentally. However, it should be emphasized that a systematic study of such properties is not pos-

sible because the values of natural lifetime or experimental broadening cannot be set in a controlled manner and are delivered as discrete values during experiments.

Another important aspect of considering high energy resolution schemes in XAS experiments is the possibility of simultaneous detection of XES spectra when recording XAS data. This is an important aspect as XES is complementary to XAS and supplements the absorption data with information on the occupied electronic state of the studied material. Two scenarios should be considered when executing high-resolution experiments. First, we should focus on the detection of core-to-core decay channels, such as K_α X-ray emission, that are characterized by a relatively high probability of decay and, consequently, high X-ray yields. Detection of core-to-core emission is also important when experimental data are to be supplemented with theoretical calculations. For core-to-core transitions, the initial and final states are easily described in a multielectron picture and therefore are easy to implement in many computing codes. In the second alternative, the XES detection can focus on K_β or even valence-to-core X-ray emission. These signals are very rich in information regarding the chemical and spin state of the studied system. However, the measured intensities are much weaker compared to core-to-core transitions, and the eventual implementation of theoretical models may require sophisticated optimization methods. We can definitively state that the high-resolution detection schemes are necessary for two reasons, namely, the determination of the valence electronic orbitals from the valence-to-core XES data and the precise determination of conduction electronic states from high-resolution XAS data. As mentioned, the latter is especially important for Cu-oxide since a weak pre-edge feature is smeared out in conventional XAS spectra due to the relatively large natural broadening of the *1s* core state.

4. Conclusions

To conclude, the surface of Cu NPs can be altered through the use of different oxidizing agents, and X-ray spectroscopy represents a perfect tool to study the near-Fermi-level electronic states, which are most sensitive to the chemical environment and local structure of the material. The studied density of states (holes and electrons) will give a clear indication of the strength of the dephasing process at the NP surface-charge acceptor interface and thus enable quantitative analysis of a range of phenomena, such as the localized surface plasmon cooling mechanisms in metal NPs. The high energy resolution experiments will help to develop rational design schemes of plasmonic nanostructures for plasmon-enhanced solar-driven chemistry.

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