Pt L_{3,2}-edge whiteline anomaly and its implications for the chemical behaviour of Pt 5d_{5/2} and 5d_{3/2} electronic states – a study of Pt-Au nanowires and nanoparticles

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Abstract. We report the L_{3,2}-edge whiteline anomaly observed in PtAu nanowire, PtAu and Pt nanoparticles deposited on Si nanowire, and their comparison with that of Pt metal. It is found that charge redistribution upon the formation of these materials can indeed be tracked with the L_{3,2} whiteline intensity. The implications of these findings are discussed.

1. Introduction

The whiteline (WL) anomaly is often referred to as the non-statistical distribution of the intensity of the sharp resonance just above the threshold of the L_{3,2}-edge absorption edge. The most well known case is the Pt L_{3,2}-edge WL anomaly in Pt metal, of which the L_{3}-edge exhibits an intense WL while the L_{2}-edge does not. This is a classic example of non-statistical distribution of L_{3,2} WL intensity, hence the distribution of the densities of states of the 5d_{5/2} and 5d_{3/2} electrons since dipole transition allows for the probing of unoccupied states of both 5d_{5/2} and 5d_{3/2}, and 5d_{3/2} only, at the Pt L_{3} and L_{2}-edge, respectively. The interpretation of this phenomenon as the result of relativistic effect and the disparity in the filling of the 5d electrons in Pt (5d_{3/2} gets filled first) was first provided by Mott.[1] He pointed out that this was because the empty 5d states in Pt metal are mainly with \( j = 5/2 \) character.

This anomaly has since been revisited on several occasions.[2-5] For example, Brown, Peierls and Stern reported that the difference in the area under the curve of the L_{3} and L_{2} edge WL can be correlated quantitatively to the 5d hole counts in Pt metal; Matthesis and Dietz extended the discussion to include d_{5/2} and d_{3/2} hole counts and correlated them to the area under the curve derived from both edges as the difference between the XANES and an arctan-like function (represented by the Au L_{3,2}-edge XANES of the Au metal). Mansour, Cook and Sayers applied this approach to derive relativistic d-hole counts in Pt metal and related systems. [4] This anomaly was also found at the M_{3,2} edge of Pt metal, confirming the non-statistical distribution of the unoccupied 5d_{5/2} and 5d_{3/2} states in Pt metal [5]. In Pt compounds, however, such as Pt(II) and Pt(IV) species, both edges exhibit WL whose intensities are closer to the statistical expectation. Thus this anomaly is associated with a nearly filled 5d band in Pt metal or related metallic Pt systems.

The advent of nanoscience and nanotechnology has prompted us to revisit this phenomenon, since many Pt and Au nanostructure systems exhibit potential for the enhancing catalytic performance. We ask whether or not this anomalous behavior is seen in PtAu nanoalloys, and if the chemistry of the 5d_{5/2} and 5d_{3/2} electrons in metallic Pt nanostructures can be tracked using Pt L_{3,2}-edge WL. We have
examined the chemical behavior of the Pt L 3,2-edge WL intensity in Pt-Au nanowire, and Pt-Au nanoparticles and Pt nanoparticles dispersed on silicon nanowires. It is found that there is a subtle but noticeable redistribution of 5d 5/2 and 5d 3/2 charges (holes) relative to Pt metal upon nano Pt-Au alloy formation. The preliminary result of this study is reported herein.

2. Experiment

The Au-Pt nanowire (NW) was prepared using a solution method as describe previously.[6] The specimens had been characterized using XRD and TEM, showing a hybrid structure of crystalline nanowires with nodules of fcc crystal structure. The dimension is on the order of 5 – 10 nm. The Pt nanoparticle (NP) and Pt-Au nanoparticle on Si specimens were prepared by an electrode-less technique.[7] A PtAu bulk alloy sample, PtAu, were also run as references. The Pt L 3,2-edge XAFS measurements were conducted at the PNC-XSD (sector 20) BM beam line of the Advanced Photon Source (APS) in transmission mode. APS operates at 100 mA in the top-up mode.

3. Results and Discussions

Figure 1 shows the XAFS of the PtAu NW at the Pt L 3,2 and Au L 3,2-edge together with the TEM image. It can be seen that the PtAu NW shows a larger Au edge jump indicating that it is Au rich. The edge jump analysis using tabulated values from McMaster et. al.[8] indicates that the atomic ratio of Au/Pt is 1.92, and more interestingly, the Pt L 2-edge exhibits no WL while the Pt L 3-edge exhibits an intense WL. In the following, the anomaly is tracked via (i) comparison of PtAu nw with Pt metal, (ii) comparison of the AuPt NW L3 intensity with that of its L2-edge and (iii) comparison of the area under the curve (WL intensity) using Au L3,2-edge as the background.

3.1 Comparison with Pt metal whitlines

Figure 2 shows the Pt L 3,2 WL of PtAu NW and that of Pt metal. It appears at first glance that the PtAu NW L 3,2-edge WL is less intense than that of the Pt metal although it is blue-shifted (+0.9 eV) and broadened (FWHM by 1.4 eV). The L 2-edge WL of PtAu NW appears more intense than that of Pt metal and exhibits the same shift to higher energy. This observation indicates that charge redistribution takes place upon the formation of PtAu NW. The difference curve between the WL of PtAu NW and Pt metal (not displayed) however shows comparable Pt L 3 WL intensity in PtAu NW relative to Pt and a small net gain in the intensity of the Pt L 2 WL indicating that d 3/2 charge is slightly depleted at the Pt site in PtAu NW. The considerable mismatches in the oscillation maxima in energy (k space) show that alloying takes place in this system (it is not core-shell). This will be discussed further below.
3.2 Difference curve between Pt L3 and L2 XANES
We use the difference curve between the Pt L3 and L2 edge XANES to obtain the difference in the area under the WL, \( \Delta A = A_3(\text{exp}) - cA_2(\text{exp}) \) where \( c \) is a scaling factor, the ratio of the edge jump between Pt L3 and L2 edge, \( A_3 \) and \( A_2 \) are the experimentally determined area under the WL. If 5d\(^{5/2}\) is the dominant component of the unoccupied DOS, \( \Delta A \) scales with the 5d\(^{5/2}\) hole counts (e.g. 0.3 from theory).[3] Figure 3 shows such a comparison. \( \Delta A \) thus obtained is \( \approx 1.4 \times 10^4 \) cm\(^{-1}\)eV in both cases.

3.3 WL intensity
The Pt WL intensity can be obtained by removing an arctan-like back ground represented by the Au L\(_{3,2}\)-edge XANES since Au has the same fcc structure as Pt and exhibits no WL. Analysis using tabulated edge jumps (2.5\times10\(^3\) cm\(^{-1}\) for L\(_3\) and 1.16\times10\(^3\) cm\(^{-1}\) for L\(_2\))[8] yields nearly identical area under the curve of \( A_3 \) of 1.43 \times 10^4 and 1.44 \times 10^4 cm\(^{-1}\)eV and \( A_2 \) of 0.35 \times 10^4 and 0.37 \times 10^4 cm\(^{-1}\)eV for Pt and PtAu NW, respectively, yielding \( h_{5/2}/h_{3/2} \) ratio of 0.29 and 0.27. This result shows that aside from for 5d\(_{5/2}\) to 5d\(_{3/2}\) charge redistribution (seen in WL shift and broadening), there is little detectable net charge count change on and off the Pt site upon PtAu NW formation compared to Pt metal.

3.4 The Au site
Since metallic gold has a nominally full d band, its WL in PtAu alloy is less sensitive unless a significant amount of d charge is depleted. However, the position of the oscillations in the XANES is informative since the progressive mismatching of the oscillations reflects whether or not Pt has an Au nearest neighbor since the \( k \) dependence of the backscattering amplitude and phase of Au is distinctly different from that of Pt even if they are both fcc with similar lattice constants. Close examination of Figure 2 and Figure 4 reveals that the oscillation maxima in the alloy occurs in between those of Au and Pt foils indicating that the nearest neighbour of Pt contains Au atom in the PtAu NW.

3.5 Pt NP and PtAu NP on SiNW
Figure 5 shows the Pt L\(_3\)-edge XANES of Pt/SiNW, PtAu/SiNW, alloy PtAu\(_6\), and Pt metal. Together with the oscillation patterns shown in Figure 2 for PtAu NW compared with Pt, the characteristic
oscillations beyond the WL reveal the following (i) all structures are fcc-like, (ii) The oscillations for Au metal appear at significantly lower $k$ than that of Pt metal, (iii) PtNP/SiNW shifts slightly to high $k$ whereas PtAu/SiNW shifts moderately to lower $k$ and (iv) PtAu NW and PtAu$_6$ both shift to lower $k$ in accordance with their stoichiometry (more dilute the sample, more significant the shift). These results indicate that Pt’s nearest neighbor contains Au, likewise Au neighbors containing Pt; more quantitative information awaits further analysis.

4. Conclusion
The results reports show that the 5d charge redistribution in metallic Pt systems can be tracked using the Pt L$_{3,2}$-edge WL anomaly. Thus it is a great tool to study the performance of catalyst.

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