

Zhang and Sham Reply: In Moriarty's Comment [1], he raised an issue with our interpretation of the XPS binding energy shifts in terms of the initial state effects [2].

Let us first note that our paper reported the preparation and electronic structure of a series of thiol-capped Au nanoparticles using a number of techniques [2] including XAFS, TEM, XRD, UV-visible, and XPS. Our interpretation of the Au binding energy was not based solely on initial state effects although the notion of a positively charged nanoparticle in the final state when the cluster was supported on a poorly conducting substrate [3–6] was not explicitly addressed. This will not affect the main conclusions of our Letter although the issues are valid and timely. We will address them below.

It is recognized that the core level binding energy depends on initial and final state effects. The final state effect in this context arises from the relaxation of the core hole, which is screened by conduction electrons in metals and polarized charge in nonconductors. Although it is common to assume that the final state effect in similar metallic systems is the same, its details are still being pursued [7]. The final state effect Moriarty alluded to in his Comment deals with how fast a small cluster can be neutralized in the spirit of the work by Wertheim *et al.* [3] and others [4–6].

Charging is an experimental problem for nonconductors and results in a shift of the spectrum to higher binding energy. This is accompanied by a linewidth broadening and a skew line shape. The issue here is whether or not the nanoparticle (NP) is neutralized fast enough upon photoemission (NP-substrate transport). It has been reported [3–6] that the Fermi level shifts to above zero binding energy in the XPS spectrum if the final state of the cluster is not neutralized within the photoemission time scale. Moriarty's comments suggested that this could be the case in the XPS of our thiol-capped Au NPs deposited on a conducting carbon substrate. We argue that this is not necessarily the case. The experimental results show only a small $4f$ shift of 0.36 eV for the smallest NP (1.6 nm), where charging should be the most severe. Also, the $4f$ peak does not show any abnormal line shape [8]. Furthermore, the valence band exhibits the trend of Au d bandwidth narrowing and band centroid shift expected for a reduction in NP size. Charging in these nanoparticles would have adversely affected the trend.

The biggest observed shift of 0.36 eV is comparable in magnitude to the surface core level shift in Au metal. The

positive shift is expected from initial state considerations and supported by other experiments [2]. The effect of charging is expected to be larger than what we observed [3].

The most interesting issue is the position of the Fermi level. To identify metallic behavior, we seek nonzero densities of states at zero binding energy in the XPS. Our statement "a Fermi edge is not noticeable in the 1.6 nm NP," is consistent with the lack of UV-visible absorption (plasmon) shown in Fig. 1(d) of [2], but is perhaps not the best way to describe the system. If charging pushes the Fermi level of the NP to slightly above zero binding energy, as Moriarty's Comment suggested, then a couple tenths of an eV will move it back to zero. Even if this was the case, the densities of states at the Fermi level did not exhibit the usual Fermi edge behavior as expected from Fermi-Dirac statistics seen in bulk metals. What could be an alternative explanation for the Fermi level shift observed in small clusters is that a pseudogap develops as the size of the NP becomes smaller, as was commonly observed in low dimensional materials, such as high T_c superconductors, which exhibit non-Fermi behavior (e.g., Luttinger liquid) at zero binding energy. Thus, we refrained from saying "the 1.6 nm NP is an insulator." It appears likely in hindsight that the conventional wisdom to identify metallic/insulator behavior of nanoparticles by seeking a Fermi edge at the zero binding energy of a photoemission spectrum is no longer adequate.

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