## Comment on "X-Ray Studies of the Structure and Electronic Behavior of Alkanethiolate-Capped Gold Nanoparticles: The Interplay of Size and Surface Effects"

In a recent Letter [1], Zhang and Sham have interpreted shifts in the binding energies of Au $4f$ and valence photoemission peaks from gold nanoparticles as arising from size-dependent lattice contraction and charge redistribution. Here we argue that the Zhang and Sham interpretation of binding energy shifts solely in terms of the initial state is flawed and that this has a particularly strong impact on their conclusions regarding the density of states at the Fermi level in Au nanoparticles.

An important consequence of the combined small capacitance and surface passivation of thiol-coated Au nanoparticles is that significant shifts in the binding energy of photoelectron peaks arise due to the "Coulomb charging" of the particle during photoemission [2–5]. That is, if the nanoparticle is sufficiently electronically decoupled from its environment, as is generally the case for thiol-passivated particles, the core hole is not neutralized on the time scale (of order femtoseconds) of the photoemission process. The core hole created via photoexcitation therefore interacts strongly with the outgoing photoelectron and increases the electron binding energy relative to that observed for a bulk material (or, indeed, a sufficiently large nanoparticle).

Zhang and Sham [1] interpret size-dependent binding energy (BE) shifts in the photoemission spectral features of Au nanoparticles as arising from electronic rehybridization and changes in Au coordination number—i.e., only initial state effects are considered. However, building on the work of Wertheim *et al.* [2], a number of groups [3–5] have explained BE shifts in photoelectron spectra from nanoparticles in terms of the final state effects described above. The key aim of this Comment is to point out that it is not possible to interpret the BE shifts of the Au $4f$ and valence spectral features solely in terms of the ground state of the nanoparticle, as suggested in [1].

The lack of consideration of final state effects has a significant impact on Zhang and Sham's interpretation of size-dependent changes in the density of states at the Fermi level. They argue that at a size of 1.6 nm the nanoparticles are associated with a negligible density of states at the Fermi level. This conclusion is based on a comparison of valence band spectra acquired for particles of various diameters. Importantly, the Coulomb potential related to the unneutralized core hole will not only affect the binding energies of core-level and valence band features but will also push the Fermi edge of the nanoparticles to higher BE [3,5]. If final state effects are not considered, then the movement of the Fermi edge can be incorrectly interpreted as a reduction in the density of states at $E_F$.

A close inspection of Zhang and Sham's valence band data does not support their conclusion that a Fermi edge

"is not noticeable" in the spectrum for 1.6 nm diameter nanoparticles. Certainly, there is little or no density of states at the "nominal" Fermi level (i.e., 0 eV binding energy) for the 1.6 nm nanoparticle spectrum. However, if one compares the near Fermi edge regions for the valence band spectra of the 2.4 and 1.6 nm nanoparticles in Fig. 4 of [1], there is an edge visible just below the 0 eV binding energy position in both cases. (The Fermi edge observed for the 4.0 nm features appears at a slightly lower BE due to the larger size of the nanoparticles [6].) We posit that this feature in each case arises from a Fermi edge density of states whose spectral signature has been shifted to higher binding energy due to the core-hole potential in the final state of the photoemission process. Zhang and Sham's conclusion that a 1.6 nm nanoparticle is "on the verge of a metal to insulator transition" is, we believe, unsupportable on the basis of their interpretation of the valence band spectra.

In summary, Zhang and Sham's consideration of the binding energy shifts of XPS spectra of Au nanoparticles solely in terms of initial state effects is flawed. A strong Coulomb interaction between the core hole and the outgoing photoelectron produces significant binding energy shifts that must be considered when interpreting the photoemission spectra of nanoparticles.

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[6] Admittedly, the relatively poor quality of the spectra in Fig. 4 of [1] does not aid identification of the Fermi edge feature. It is not immediately apparent why the authors used x-ray photoemission spectroscopy (XPS) rather than UPS (ultraviolet photoelectron spectroscopy) to measure the valence band spectra—the photoionization cross sections for valence states are substantially higher for UPS.