

## Detection of Quantum Confined States in Au Nanoclusters by Alkali Ion Scattering

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Charge state-resolved time-of-flight spectra were collected for 2.0 keV  $^{23}\text{Na}^+$  scattered from Au nanoclusters deposited on  $\text{TiO}_2(110)$ . The neutral fraction of Na scattered from metallic Au is low ( $\sim 3\%$ ), but it is surprisingly high (up to 50%) for small clusters. The results demonstrate that alkali ions couple to electronic states specific to the nanoclusters, and that the energy of the states is a function of the nanocluster size. This technique provides a new method for the spectroscopy of nanomaterials.

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Nanostructures behave as isolated quantum mechanical systems because of their finite size [1–3]. This novel behavior has opened the door to new technologies, such as single-electron transistors and molecular computers [4–6]. Much of the current research effort has been to develop methods for fabricating nanomaterials and to characterize their size distributions and morphology. There are, however, many open questions about the basic physics of materials on the nanoscale, particularly with respect to their electronic properties, which must be understood in order to fully exploit their potential.

The quantum-size behavior of nanomaterials also enables their use as catalysts for specialized chemical processes. For example, small Au nanocrystals can oxidize CO and hydrocarbons at room temperature and below, despite Au itself being an inert metal [1,7]. This unusual behavior presumably results from interaction of species chemisorbed at the surface with electronic states specific to the nanocrystals. To understand the catalytic behavior at a fundamental level, it is necessary to determine the localized electronic structure and how it depends on the size and shape of an individual nanoparticle.

The confined states in nanoparticles are difficult to detect directly, however, as most techniques cannot distinguish the signal arising from the cluster from that of the supporting substrate [8]. Although x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy can distinguish cluster and substrate innershell electrons spectroscopically, these techniques provide no information concerning the important states near the Fermi level. Ultraviolet photoelectron spectroscopy (UPS) can detect valence states, but it is not specific to the clusters, particularly if the signal from the nanoparticles is much weaker than from the substrate [9]. Scanning tunneling spectroscopy (STS) can specifically measure the electronic structure localized at the clusters, but it is limited to states extremely close to the Fermi level and can be used only with certain types of materials. In this Letter, we present a new experimental method for probing the electronic structure of nanomaterials in which neutralization during alkali ion scattering is used

to detect the confined states. The method is illustrated for Au nanoclusters grown on  $\text{TiO}_2(110)$ . We show that alkali ion scattering provides information specific to nanomaterials that complements the findings of other techniques.

Low energy ion scattering is a well-established method for surface analysis in which the energy of the scattered particles provides the mass distribution of surface species [10,11]. It has also been shown that neutralization in low-energy alkali ion scattering is sensitive to the electronic states near the Fermi level [12–14]. In particular, the neutral fraction (NF) of scattered alkali ions depends on the local electrostatic potential directly above the scattering site [13–16]. For certain surfaces in ultrahigh vacuum (UHV), there are particular electronic states that overlap the alkali ionization level, in which case the neutralization is directly correlated to these surface states. An example of this is  $\text{Li}^+$  scattering from clean silicon, where the projectile ionization level couples to localized surface dangling bonds during scattering, rather than to delocalized bands [14]. Calculations have also suggested that ion scattering can detect confined states in a 2D thin film [17], but this has not yet been observed experimentally.

The measurement described here is the first to directly probe the confined states of nanoclusters by ion scattering. Ions that have impacted the cluster are differentiated from those that have hit the substrate by their scattered energy, while the interaction is limited to the outermost atomic layer of the nanocrystal by using a large scattering angle and a normal incidence direction [11,13]. A remarkable enhancement of the neutralization probability for small clusters is found, which can be explained only as charge transfer from states localized within each individual nanoparticle.

The  $\text{TiO}_2(110)$  single crystal substrate ( $8 \times 8 \times 1 \text{ mm}^3$ , Commercial Crystal Laboratories) was attached to a Ta holder, and loaded onto an XYZ rotary manipulator in an UHV chamber (base pressure =  $5 \times 10^{-11}$  Torr). An infrared pyrometer was used to measure the sample temperature, which was calibrated by a thermocouple attached to the edge. The surface was prepared

by cycles of ion bombardment and annealing (500 eV Ar<sup>+</sup> for 30 min, followed by a 15 min anneal at 975 K) until a sharp (1 × 1) low-energy electron diffraction pattern was obtained [18].

Nanocrystals with diameters ranging from 1 to 100 nm were grown by deposition of Au onto the TiO<sub>2</sub>(110)-(1 × 1) surface following recipes from the literature [7,19–21]. The evaporator consisted of Au wire (99.999%, Alfa Aesar) wrapped around a W filament (Mathis). Au was deposited at a rate of ~1.0 Å/min, as calibrated with a quartz crystal microbalance. All depositions (and ion scattering measurements) were performed with the sample at room temperature. The purity of the sample was checked with XPS immediately after cleaning and again following the deposition of Au. After each NF measurement, the Au/Ti ratio was checked by measuring the kinetic energy distribution of scattered 2.0 keV <sup>23</sup>Na<sup>+</sup> ions with an electrostatic analyzer, as in traditional ion scattering spectroscopy (ISS) [20,21]. The data showed that the Au initially grows in 2D islands, but the islands become 3D after a coverage of ~0.15 monolayers (ML). Following the largest deposition, no Ti signal was observed in either ISS or XPS, indicative of the formation of a thick Au film.

Time of flight (TOF) was used to measure the charge state-resolved kinetic energy distribution of the scattered ions. The 2.0 keV <sup>23</sup>Na<sup>+</sup> beam was deflected across a 1.0 mm<sup>2</sup> aperture to produce 40-ns pulses at a rate of 80 kHz. The beam was incident normal to the surface, and the ions and neutrals scattered at 150° were detected by a microchannel-plate (MCP) array after traveling through a 0.55 m long flight tube containing a pair of stainless steel deflection plates. “Total yield” spectra were collected with the deflection plates held at ground, while “neutrals only” spectra were collected by placing 300 V between the plates to deflect the scattered ions.

Figure 1 shows representative TOF spectra collected by scattering 2.0 keV Na<sup>+</sup> from Au grown on TiO<sub>2</sub>. The spectra are displayed with respect to flight time, with longer times corresponding to lower scattered energies. Each spectrum is dominated by a single scattering peak (SSP), which represents Na particles that have suffered a single binary elastic collision with a Au surface atom. Note that the kinetic energy of Na scattered from the lighter Ti and O atoms in the substrate would be too low to be detected by the MCP. The combination of normal incidence and a large scattering angle ensure that a majority of the emitted ions are singly scattered [11]. The few multiply scattered projectiles show up as a broad background with energies mostly below the Au SSP.

The NF of the singly scattered Na particles was determined by dividing the “neutrals” SSP by the total yield SSP. A background was subtracted, as depicted by the dashed lines in Fig. 1, and the SSP areas were then determined by integration. The shaded areas in Fig. 1 show how the single scattering region was typically chosen. Note, however, that the calculated NF is not

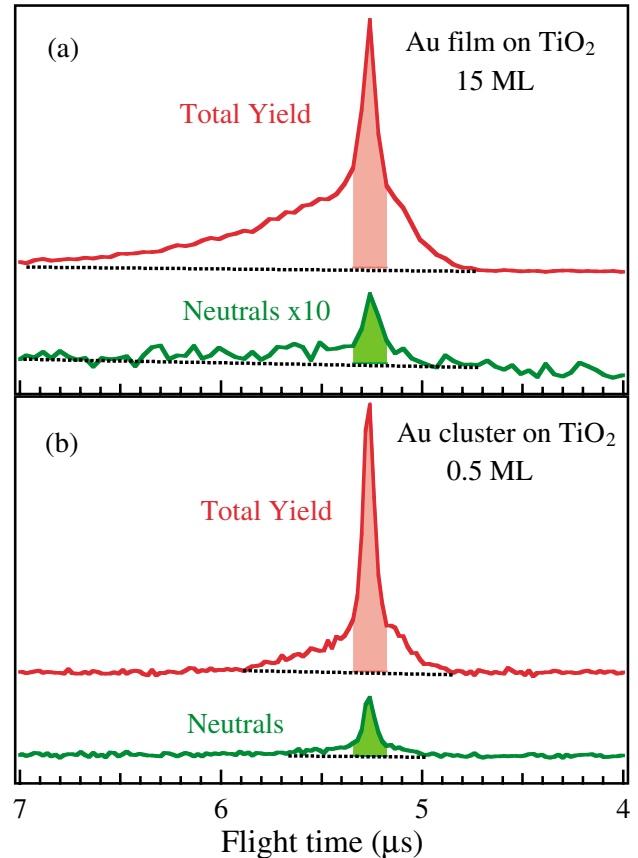


FIG. 1 (color online). TOF spectra of the total and neutral yields collected at a 150° scattering angle for normally incident 2.0 keV <sup>23</sup>Na<sup>+</sup> scattered from (a) a Au film, and (b) Au clusters on TiO<sub>2</sub>(110). Dashed lines indicate the backgrounds used in the analysis, and the integration areas are shaded.

very sensitive to the specific details of this procedure—the change to the NF was minimal even if the entire areas between the peaks and backgrounds were integrated so as to include a significant contribution from multiple scattering. Nevertheless, the inaccuracy in assigning the integration region was incorporated along with the statistical error in determining the error bars shown in Fig. 2.

Figure 2 displays the NF as a function of the average Au coverage, where 1 ML refers to the number of atoms in a close-packed layer (~2.6 Å thickness) [19]. An increased Au coverage corresponds to the formation of larger Au clusters. The NF in scattering from the smallest clusters is on the order of 50%, and it decreases with increasing Au deposition, reaching a limiting value of about 3% for the highest coverage, which corresponds to scattering from a bulk Au film. Note that there are fewer scattered Na particles and correspondingly larger error bars for the smallest clusters.

The very small NF for the Au film can be explained by considering that the work function of a Au surface (5.10 eV) is very close in energy to the ionization level of Na (5.14 eV). When the Na ion moves close to the Au surface, the 3s level shifts up and broadens due to the image charge and finite interaction time [12], as depicted

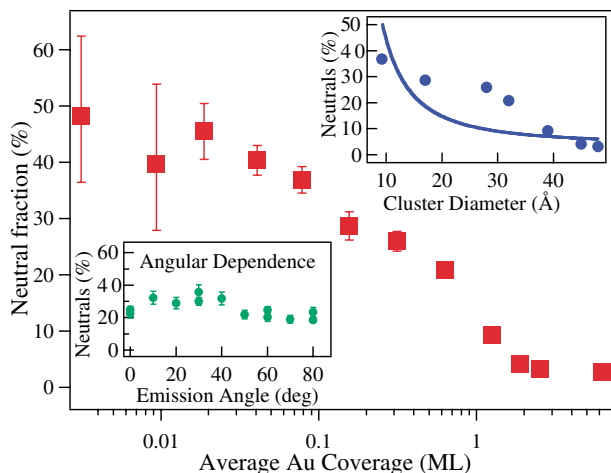


FIG. 2 (color online). Neutral fractions of singly scattered 2.0 keV Na ions shown as a function of the average Au coverage. The right side inset shows NF vs cluster diameter, with the symbols indicating experimental data and the solid line a theoretical fit (see text). The left side inset shows NF for  $\text{Na}^+$  scattered from a 0.15 ML Au coverage as a function of the emission angle with respect to the surface normal.

in Fig. 3(a). Because the Na level lies predominantly above the Au Fermi level when near the surface, the NF is very small.

The large NF associated with the smaller Au clusters suggests that electronic states specific to the nanoclusters participate in the neutralization. Previous work has indicated that confined states are indeed present in small Au clusters, and that these states are at least partially filled. STS observed a size effect correlated to the catalytic activity of small clusters [1]. Discrete confined states positioned near the Fermi level of bulk Au were mea-

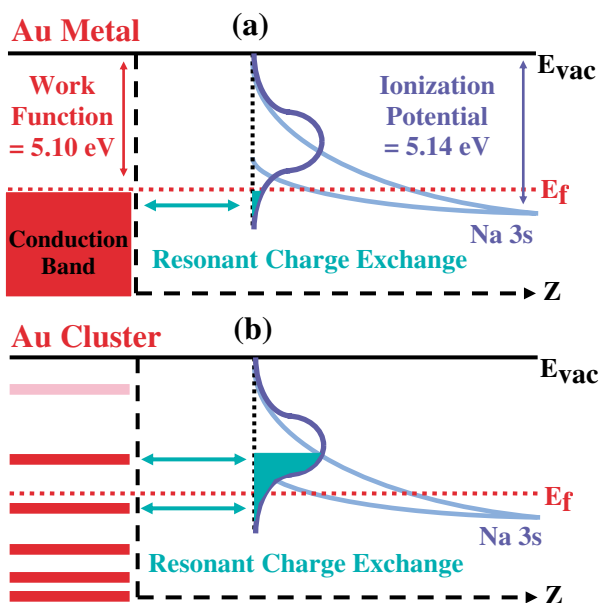


FIG. 3 (color online). Schematic diagram of resonant charge exchange between the Na 3s level and (a) the conduction band of Au metal, and (b) the confined states in Au nanoclusters.

sured with photoemission from negatively charged gas-phase  $\text{Au}_{20}$  clusters [3]. Size-selected small monodispersed  $\text{Au}_n$  ( $n \leq 20$ ) gold clusters supported on magnesia were studied by temperature-programmed reactions and first-principle simulations, and partial electron transfer from the surface to the gold cluster was shown to play an essential role in the catalytic activation of gold clusters [22]. If Au clusters on  $\text{TiO}_2$  were at least partially negatively charged, then states above the Fermi level of metallic Au would be filled. Such localized states are indicated schematically in Fig. 3(b), which shows how they would overlap a broadened and shifted Na level, leading to a large NF. In the case of clusters, the upward shift may be due to a combination of image charge and interaction with negative charge in the clusters.

To illustrate the interaction of Na ions with the confined states of small nanocrystals, a simple estimate was made of the NF vs cluster size. First, the relationship between the average Au coverage and the cluster size measured by STM [7] was used to plot the NF vs cluster diameter shown by the circles in the right side inset of Fig. 2. Next, the energy of the highest occupied state as a function of cluster diameter was taken from UPS measurements of negatively charged gas-phase Au cluster ions, which showed a smooth evolution with size from less than 2.5 eV for the smallest clusters to the work function of bulk Au [23]. Note that states due simply to quantum confinement of electrons would also increase their energy with cluster size [24]. Finally, Na was scattered from a Au film as a function of Cs deposition to experimentally determine the dependence of the NF on work function. The energy of the highest occupied state was then substituted for the work function to obtain the solid line in the right side inset of Fig. 2.

This calculation provides a reasonable estimate of the overall magnitude of the effect, and it shows the correct trend in that the NF increases with smaller cluster sizes. The shape of the curve does not precisely reproduce the experimental data, however, and a number of factors contribute to this deviation. For example, with this growth method there is a distribution of cluster sizes at any given Au coverage [25], so that data represent an average over many sizes. Thus, the experimental points do not change as rapidly as the calculation would suggest. Note that this can be overcome in future experiments by utilizing nanoparticles grown by chemical methods [26]. Also, the estimate of the energy of the highest filled state in the calculation was taken from gas-phase clusters. The supported clusters in this work have different shapes, and may also interact electronically with the substrate. In particular, 2D islands are dominant for Au coverages below 0.15 ML so that the calculated diameters of less than  $\sim 20$  Å are not meaningful. Since the data in Ref. [23] involved only cluster diameters above 6 Å, the first four data points in Fig. 2 are not displayed in the right side inset. Also, the density of electronic states in clusters differs from that in bulk Au, which could affect the

assumed dependence of NF on work function taken from the Cs deposited film. Nevertheless, the experimental data do provide information that directly reflects the electronic properties of the nanocrystals. Furthermore, it is clear that a comprehensive theoretical understanding can be developed that will not suffer from the limitations of the estimate presented here.

Note that it could be argued that the high NF reflects the surface roughness and not the electronic structure of the nanoparticles. The effect of surface roughness was explored using a polycrystalline Au foil. A flat surface was prepared by sputtering with 1 keV Ar<sup>+</sup> and annealing to 800 K in vacuum. An atomic force microscopy (AFM) measurement of this surface indicated a mean roughness of 0.198 nm, which is about half of the Au atomic height. The surface was then progressively roughened by 1 keV Ar<sup>+</sup> ion bombardment (1 mA for 5, 30, 120, and 720 min). Following the longest sputtering time, AFM showed a mean roughness of 1.486 nm, or about the height of five Au atoms. Measurements of both the surface work function ( $5.10 \pm 0.15$  eV) and the scattered Na NF ( $3.5\% \pm 0.5\%$ ) showed no change with roughness, however, which demonstrates that the roughness of the cluster-covered surface by itself cannot explain high NF found for small Au clusters.

It was also found that the NF is independent of the emission angle, in contrast to ion neutralization from metallic surfaces. The left side inset of Fig. 2 shows the angular dependence of NF for Na scattered from 0.15 ML Au on TiO<sub>2</sub>(110). For a metal in which the ionization level couples to delocalized bands, the NF depends exponentially on the inverse of the perpendicular component of the outgoing velocity [12,13]. For isolated nanoparticles, however, the coupling is more atomlike, and, hence, it is angular independent.

The work reported here shows that scattered keV alkali ions couple directly to electronic states specific to the nanoclusters, providing a unique tool for probing the confined states. The NF contains direct information concerning the highest occupied confined state in a nanoparticle. It is expected that calculations of ion neutralization that specifically consider these states will be developed so that the nanoparticle electronic structure could be determined directly from the measured NF. Further measurements of the velocity dependence of the scattered particles will yield information on the dynamical properties of nanoparticle electronic interactions. This technique can also be expanded to yield unique information on other supported nanocrystals, chemically synthesized nanoparticles, and nanomaterials in diverse media.

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