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### Elucidating the electronic structure of supported gold nanoparticles and its relevance to catalysis by means of hard X-ray photoelectron spectroscopy

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#### 1. Introduction

At this point in time it has been well-established that whereas bulk gold is catalytically inert, gold nanoparticles <10 nm diameter supported onto metal oxides can be highly catalytically active for a number of reactions, including low temperature CO oxidation [1], water gas shift (WGS) [2], and NO reduction [3], and also selective for important oxidation and hydrogenation reactions where selectivity is crucial, e.g. propene to propene oxide [4] and 1,3 butadiene to 1-butene [5], respectively. However, the origin of the nanoscaling effect on catalysis by gold (Au) is still debated [6]. The leading explanations for enhanced activity are depicted schematically in Fig. 1 and are enumerated in Table 1, a list to which we shall refer throughout this work in discussing the possible origins of catalytic activity.

In short, there are two general classifications of nanoscale effects, those that are predominantly geometric in nature and those that are electronic in nature. The predominantly geometric effects have to do with the physical orientation of Au atoms that can change with size [7, 8], shape [8–11], lattice strain [11,12], and the Au-support perimeter [7]; while the predominantly electronic effects can arise from charge

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#### ABSTRACT

We report on the electronic structure of Au (gold) nanoparticles supported onto TiO<sub>2</sub> with a goal of elucidating the most important effects that contribute to their high catalytic activity. We synthesize and characterize with high resolution transmission electron microscopy (HRTEM) 3.4, 5.3, and 9.5 nm diameter TiO<sub>2</sub>-supported Au nanoparticles with nearly spherical shape and measure their valence band using Au 5d subshell sensitive hard X-ray photoelectron spectroscopy (HAXPES) conducted at Spring-8. Based on density functional theory (DFT) calculations of various Au surface structures, we interpret the observed changes in the Au 5d valence band structure as a function of size in terms of an increasing percentage of Au atoms at corners/edges for decreasing particle size. This work elucidates how Au coordination number impacts the electronic structure of Au nanoparticles, ultimately giving rise to their well-known catalytic activity.

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transfer to/from the support [13–18], or from quantum size effects [19–22].

With so many proposed explanations for the high activity of small supported gold nanoparticles, an approach is needed to experimentally disentangle these effects and assess which of these are dominant in contributing to catalytic activity; not a trivial undertaking as many of the effects are correlated with one another.

Critical to sorting out these effects is understanding the valence band electronic structure of supported Au nanoparticles. This, along with detailed knowledge of the physical structure of the nanoparticles regarding size and shape, can be particularly helpful in understanding trends in catalysis [23–26]. This approach has been applied in the field of catalysis over a wide range chemical and electrochemical reactions, e.g. the oxygen reduction reaction (ORR) in fuel cells [27] and CO oxidation in conventional heterogeneous catalysis [24].

To this end, a number of studies have measured the valence band electronic structure of Au nanoparticles supported onto  $TiO_2$  [19,28],  $Al_2O_3$  [29], and NiO [16] using ultraviolet photoelectron spectroscopy (UPS, ~40 eV) and Au nanoparticles supported onto carbon [30–33] using conventional Al K $\alpha$  X-ray photoelectron spectroscopy (XPS, 1486 eV). UPS and conventional XPS have been valuable in understanding the electronic structure of Au nanoparticles. One key point resulting from these studies is that a metal-insulator transition occurs as a function of size, observed between Au<sub>55</sub> and Au<sub>33</sub>, ascribed to quantum

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#### **Geometric Effects**



Fig. 1. Nanoscaling origins of Au catalysis. Schematic showing possible nanoscale origins of gold catalysis. Red atoms in 1a and 1b indicate undercoordinated atoms. Red atoms in 3 indicate perimeter sites.

size effects. However, UPS and conventional XPS have their limitations, as it has been found that for many supports the main spectral features of the Au d-band are generally difficult to distinguish as the nanoparticle size decreases or as gold coverage decreases, due to a heavy background valence band signal from the support that overlaps with the signal from the Au nanoparticles [16,19,28–30].

Another means to study Au d-band structure is through electronic structure theory calculations. Density functional theory (DFT) calculations have revealed that undercoordinated gold atoms have d states that are higher in energy than their corresponding full coordinated bulk gold atoms [10] and thus bind adsorbates such as O<sub>2</sub> more strongly. This provides a compelling explanation for the enhanced CO oxidation activity of small gold nanoparticles.

Given the importance of a catalyst's electronic structure in determining its catalytic activity, there remains a critical need to measure the valence band of gold nanoparticles in a manner uninhibited by the metal oxide support signal, and with high-energy resolution. We accomplish this by using an unconventional form of XPS, the hard X-ray (8 KeV) photoelectron spectroscopy (XPS) beam-line (BL47) at the Spring8 Synchrotron. Due to the proportionately large photoionizaiton crosssection of the Au 5d subshell versus those of the metal oxide support at this photon energy, we are able to straightforwardly deconvolute

#### Table 1

Leading nanoscaling effects in gold catalysis.

The nanoscaling effects are broken down into geometric and electronic effects, each with selected references from the literature that support the importance of the effect.

Geometric effects		Associated references
<ol> <li>Exposing catalytically active/undercoordinated gold sites by changing:</li> <li>Lattice strain</li> <li>Unique gold/support perimeter sites</li> </ol>	a. Size b. Shape	[7,8] [8–11] [11,12] [7]
Electronic effects		
4. Charge state 5. Quantum size		[13–18] [19–22]

any signal from the metal oxide support in the valence band that could otherwise overwhelm the valence band signal from a submonolayer of Au nanoparticles. Our study also employs DFT calculations to help interpret the spectral features that we observe. For our studies, we chose  $TiO_2$  as a support since it is known as one of the more active supports for Au nanoparticle catalysis and does not contribute to CO oxidation on its own [34]. In this manuscript, we aim to fill the gaps in our current knowledge within the area of Au nanoparticle catalysis by addressing the following two key questions for Au nanoparticles supported onto  $TiO_2$ : (1) How does the physical structure of the Au nanoparticles, e.g. size, shape, and lattice constant/strain, influence its valence band electronic structure? (2) How can knowledge of the electronic structure help sort out the different possible origins of catalytic activity, and help determine which are most important within our system of study?

Our approach to answering these questions is outlined here. We started by synthesizing size-controlled Au nanoparticles onto a flat, well-defined, conductive TiO<sub>2</sub> support by means of a ligand-free synthetic method in an effort to avoid organic contaminants. Highresolution transmission electron microscopy (HRTEM) was used to measure the size, shape, and lattice constant/strain of the supported gold nanoparticles. With detailed knowledge of these physical characteristics, we then measured the electronic structure of the Au nanoparticles by means of hard X-ray (~8 KeV) photoelectron spectroscopy (XPS). With this incident photon energy, the ratio of the absorption cross-section for the valence 5d electrons of gold to the photoionizaiton cross-section for the O 2p and Ti 3d valence electrons from the TiO<sub>2</sub> support is predicted (Fig. 2) to be an order of magnitude greater than with conventional Al K $\alpha$  X-rays at 1486 eV (~1500 eV), and two orders of magnitude greater than with UV photons (~40 eV) [35]

Using hard X-rays allowed us to see an enhanced signal from gold versus the background TiO<sub>2</sub>, which to the best of our knowledge has not yet been reported for catalytically relevant oxide supported gold nanoparticles. Based on our findings described below, we believe that selectively probing 5d transition metal catalysts on oxide supports could become very important to achieve the objective of

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