Size-selectivity in the oxidation behaviors of Au nanoparticles

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Introduction

Gold: does not oxidize,
cannot adsorb most molecules from the gas phase.

Metal oxide-supported gold particles, (less than 5 nm) have remarkable catalytic properties

Oxide shells formed on metallic entities can show high catalytic activities towards the oxidation of CO

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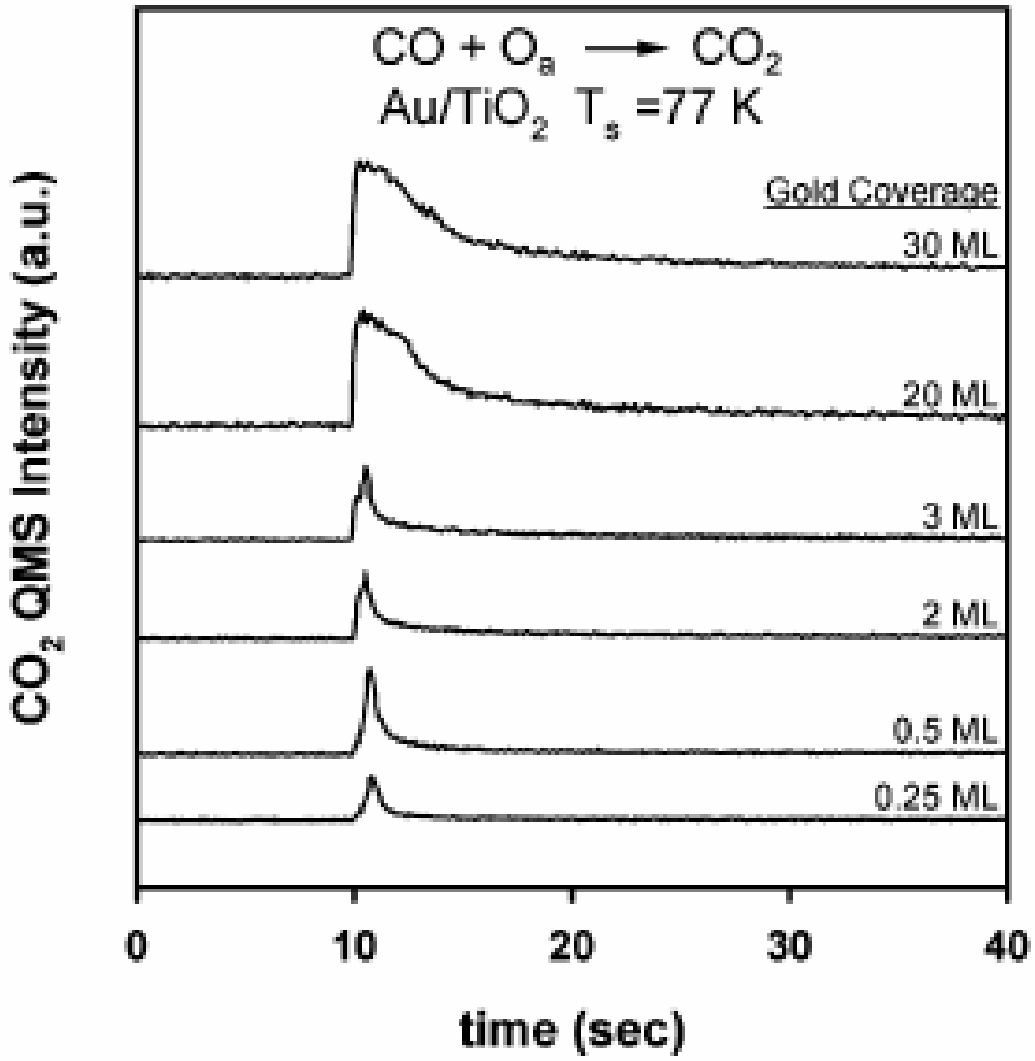
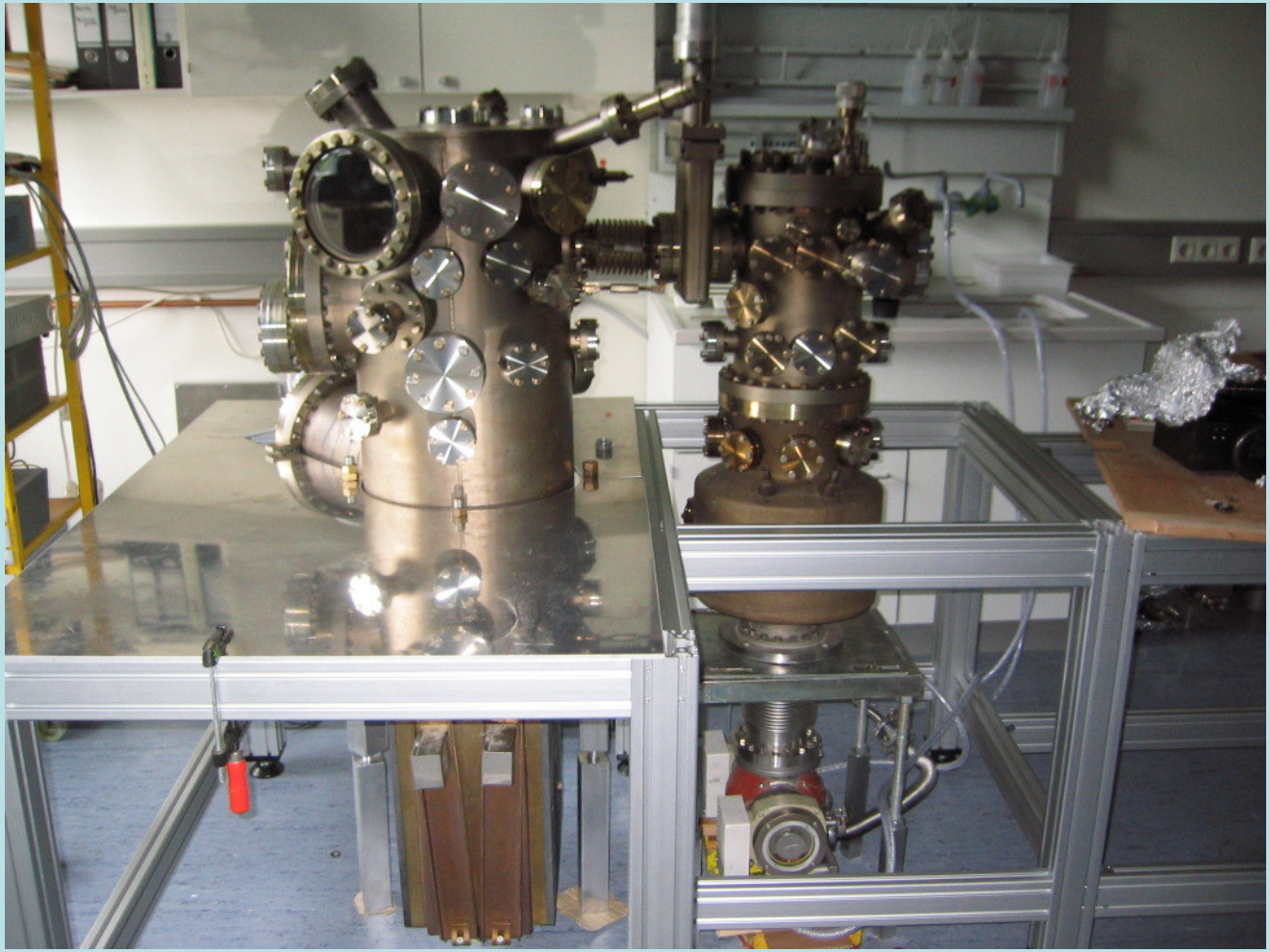
Size selectivity in a heterogeneously catalyzed reaction



Evolution of CO_2 from various amounts of gold on TiO_2 at 77 K.

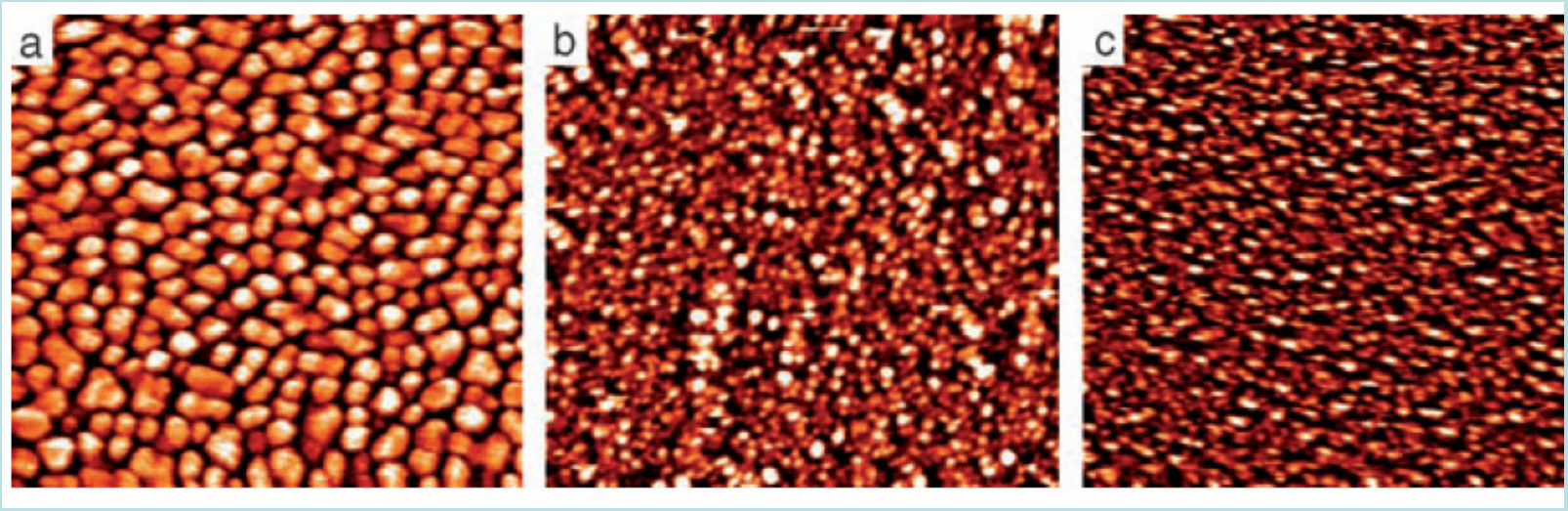
JACS, 2003, 125, 2018.

Experimental



Two ultrahigh vacuum (UHV) chambers were used for the STM and XPS studies. A sample could be transferred between the two chambers by using a portable UHV system. The polycrystalline Si wafer samples with native oxide layers were inserted into the UHV system and degassed at about 800 K, which also reduced the amount of carbon impurities. The cleanliness of the Si wafers was confirmed by using XPS (X-ray source: Al Kα, photon energy=1486.6 eV). Au nanoparticles were grown by evaporating an Au rod (purity 99.999% from Alfa Aesar) through heating either resistively or using an electron bombardment heater.

Results



4 nm

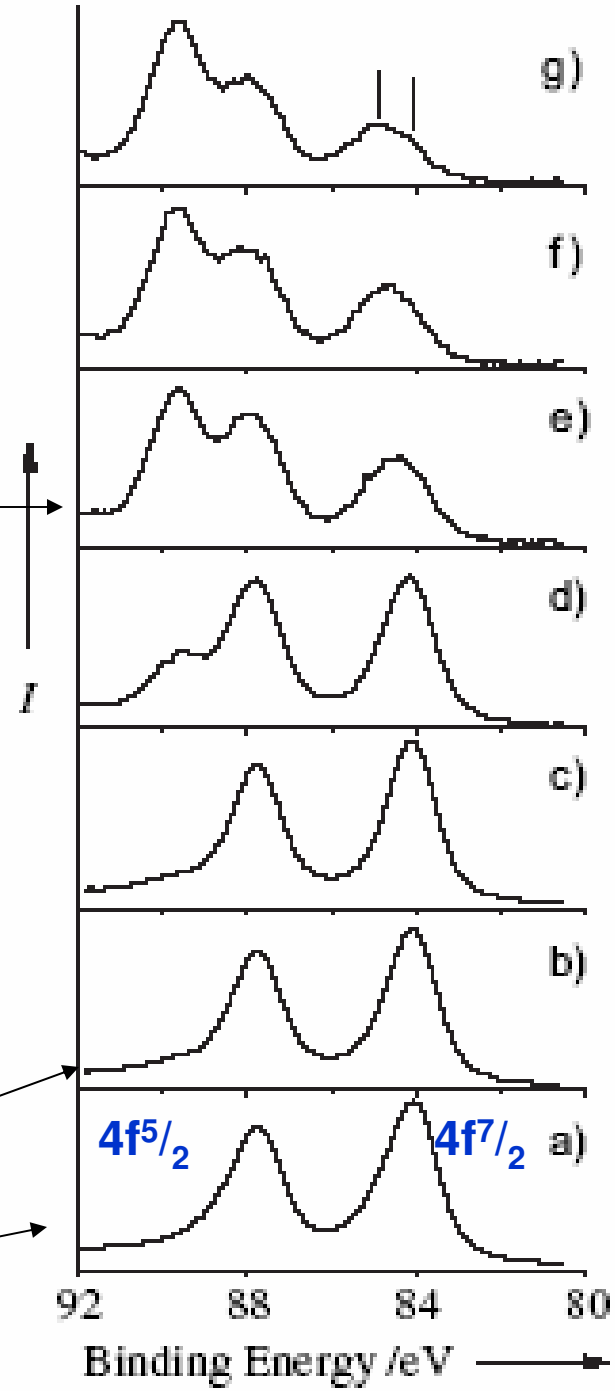
1 nm

0.7 nm

STM images

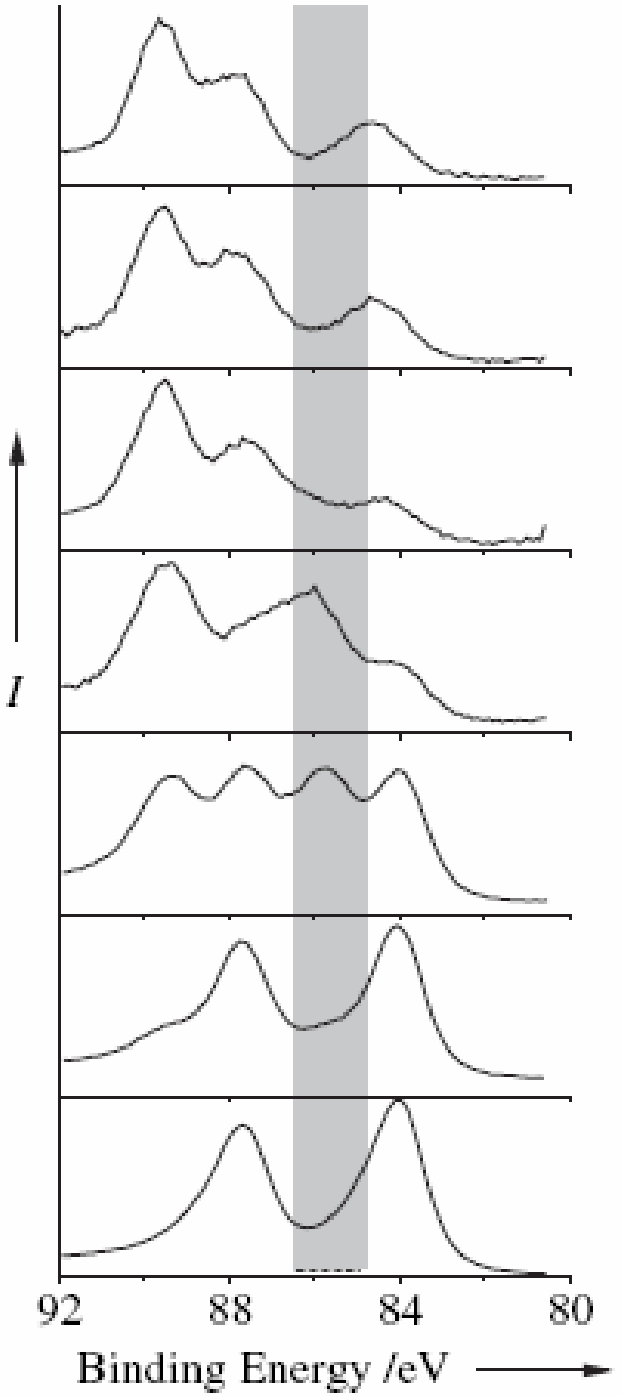
XPS spectra

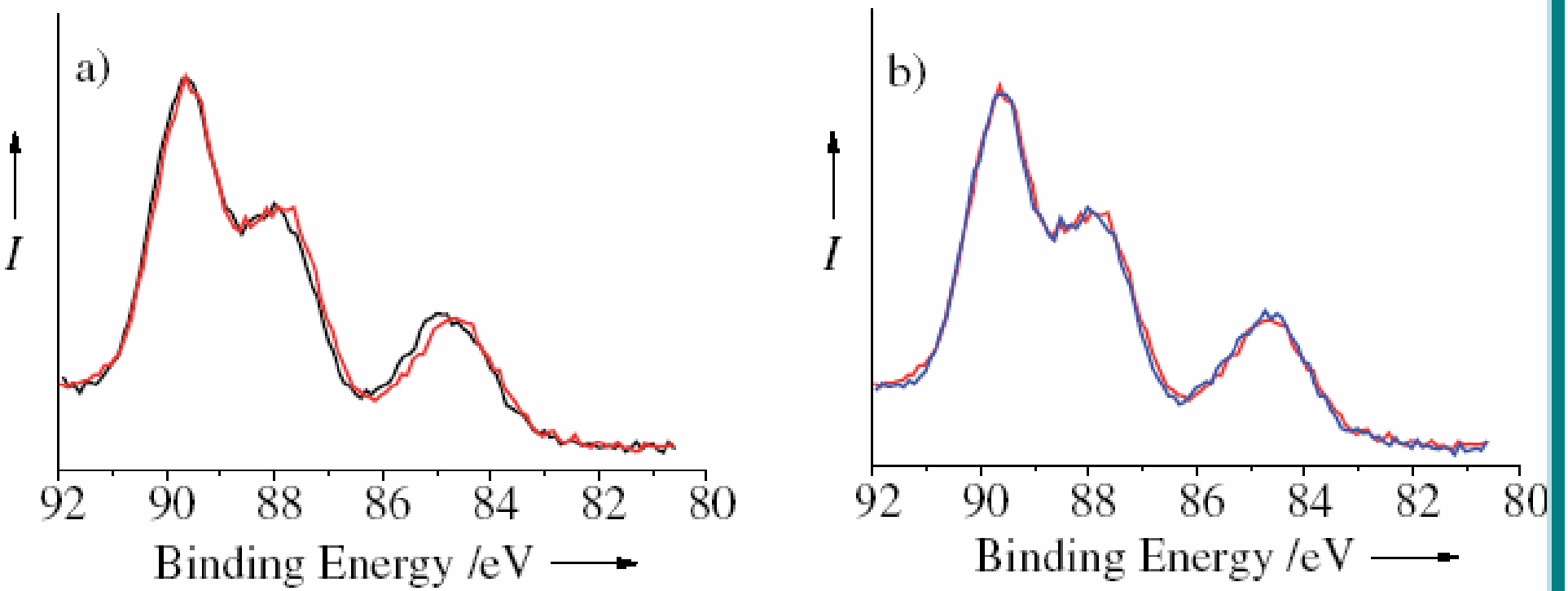
XPS spectra of the Au 4f states for Au nanoparticles grown on SiO_2/Si. The average particle size decreases, from (a) to (g).



XPS spectra

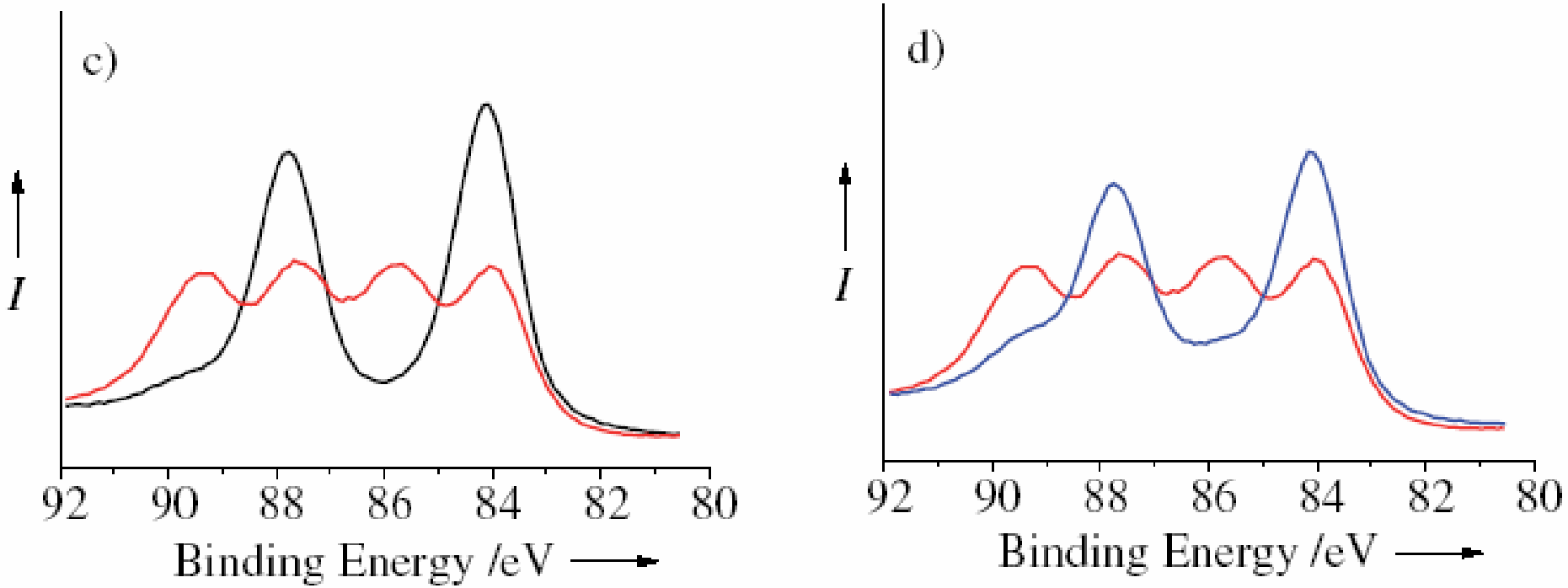
XPS spectra of the Au 4f states of the samples shown, after exposing to the atomic oxygen atmosphere.





(a)The sample of Figure 1g was exposed to the atomic oxygen atmosphere, and the Au4 f spectra were recorded before (black) and after (red) exposure to atomic oxygen.

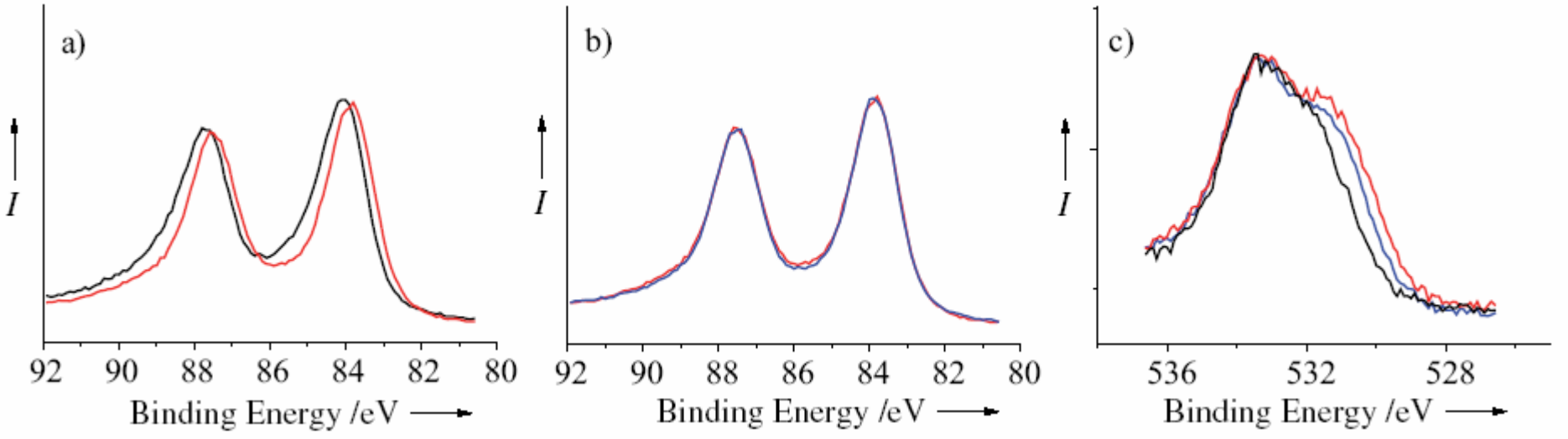
(b)The sample of Figure 1g exposed to atomic oxygen (red) was further exposed to 3000 L CO (blue).



c) The sample of Figure 1c was exposed to the atomic oxygen atmosphere, and the Au 4f spectra were recorded before (black) and after exposure to atomic oxygen (red).

d) The sample of Figure 1c exposed to atomic oxygen (red) was further exposed to 3000 L CO (blue).

Au on HOPG (Highly ordered pyrolytic graphite



a) Au 4f spectra of Au nanopartic les on HOPG before (black) and after (red) exposure to atomic oxygen.
b) The Au particles treated with atomic oxygen (red) were subsequently exposed to CO (blue).
c) The O 1s spectra were collected for the Au nanoparticles on HOPG exposed to atomic oxygen (red), and subsequently to CO (blue).

The O 1s signal from Au nanoparticles (large size) on HOPG decreases in intensity by about 30 %upon exposure to 3000 L of CO

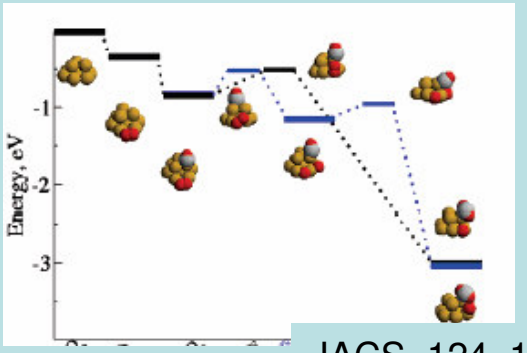
For small Au nanoparticle, it is about 0.01 %

The negative shift in the Au 4f level is due to adsorption/absorption of of Oxygen

The behaviour of small nanoparticle is substrate independent

Conclusions

Once oxygen molecules are dissociated on Au nanoparticles, they can readily react with CO to form CO2 well below room temperature.



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In contrast, present study shows… oxygen species formed by deposition of atomic oxygen on Au nanoparticles that hardly react with CO at room temperature.

Small nanoparticle studied here almost behave like bulklike Au surfaces.

This less reactive oxygen species can be either the subsurface oxygen or surface oxygen species, which are not active for CO oxidation (either they occupy the same adsorption sites as CO, thus preventing CO chemisorption on Au nanoparticles, or the Au-O interaction is too strong).

Low temperature oxidation reaction and its size dependency

Chemistry of clusters, carbon nanotube composite materials

Electrical bias on the composite material

THANK YOU

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