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Modification of the Size of Supported Clusters by Coadsorption of an Organic Compound: Gold and L-Cysteine on Rutile TiO₂(110)

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ABSTRACT: Using X-ray photoelectron spectroscopy we studied the coadsorption of the amino acid L-cysteine and gold on a rutile TiO₂(110) surface under ultrahigh vacuum conditions. Irrespective of the deposition order, i.e., irrespective of whether L-cysteine or gold is deposited first, the primary interaction between L-cysteine and the gold clusters formed at the surface takes place through the deprotonated thiol group of the molecule. The deposition order, however, has a profound influence on the size of the gold clusters as well as their location on the surface. If L-cysteine is deposited first the clusters are smaller by a factor two to three compared to gold deposited onto the pristine TiO₂(110) surface and then covered by L-cysteine. Further, in the former case the clusters cover the molecules and thus form the outermost layer of the sample. We also find that above a minimum gold cluster size the gold cluster/L-cysteine bond is stronger than the L-cysteine/surface bridging oxygen vacancy bond, which, in turn, is stronger than the gold cluster/vacancy bond.
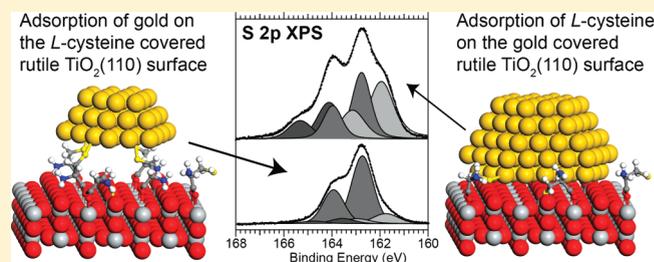
1. INTRODUCTION

Although gold is known to be the most inert metal[1] and hence is considered as catalytically inactive, Haruta et al. have shown that small gold clusters on certain oxides have a high catalytic activity for a number of different chemical reactions.[2] Special attention has been devoted to gold clusters supported by TiO₂, since they are active for the CO oxidation reaction already at low temperature if the clusters have a size of a few nanometers.[3] However, when the gold clusters are exposed to a mixture of the reactant gases their catalytic activity is lowered rapidly due to sintering.[4,5] This is a formidable challenge for the use of gold clusters as catalysts. Several methods for stabilizing metal clusters have been discussed, such as alloying, encapsulation in oxides, formation of core—shell structure, and embedding in mesoporous structures.[6] An alternative approach, which recently has been discussed in particular in relation to "green chemistry"[7] but which also has been a standard concept in colloidal research for a long time,[8] is the protection of gold clusters by thiol ligands. Capped gold clusters are considerably more stable than uncapped ones[7] and could be suspected to be quite unreactive. However, it has been shown that they may either retain a considerable degree of catalytic activity or be reactivated by a partial decapping.[9,10] Here, we take the idea of thiolate protection of clusters as the starting point for a study of how gold clusters on TiO₂ are modified by the coadsorption of a small thiol. The thiol of choice is L-cysteine (cf. Figure 1), since this amino acid contains not only a thiol group but also a carboxylic group, which is known to be an excellent molecular anchor to oxide surfaces. L-Cysteine can therefore be expected to act as a linker between the oxide support and the gold clusters as well as a spacer in between the gold clusters.

The work builds on a previous publication of ours concerned with the adsorption of L-cysteine on the rutile TiO₂(110) surface. We found that the L-cysteine molecules bind to the 5-fold-coordinated surface Ti atoms through their deprotonated carboxylic groups. Further, we suggested that an interaction of the bridging oxygen vacancies with adjacent molecules leads to a deprotonation of the molecules' thiol group and to formation of a bond between the vacancies and thiolates.[11] In this context it should be mentioned that the relative importance of bridging oxygen vacancies in comparison to that of titanium interstitials has been debated lively recently.[12−15] Recent theoretical work suggests that both types of defects may affect the surface's electronic structure and its interaction with gold clusters in a very similar way.[16,17] Further, it should also be noted that the state of the surface TiO₂(110) surface, which includes in particular the presence, nature, and type of defects, will have a profound influence on the sintering characteristics of deposited gold clusters (see, e.g., ref 18).

Here, we present X-ray photoelectron spectroscopy (XPS) results concerned with the coadsorption of L-cysteine and gold clusters on the rutile TiO₂(110) surface. The results provide information on the interaction between all three components—TiO₂(110), gold clusters, and L-cysteine. Most interestingly, we find that the order of deposition, i.e., first deposition of L-cysteine and then gold or vice versa, has a profound influence on the structure of the metal—organic film and the size of the gold
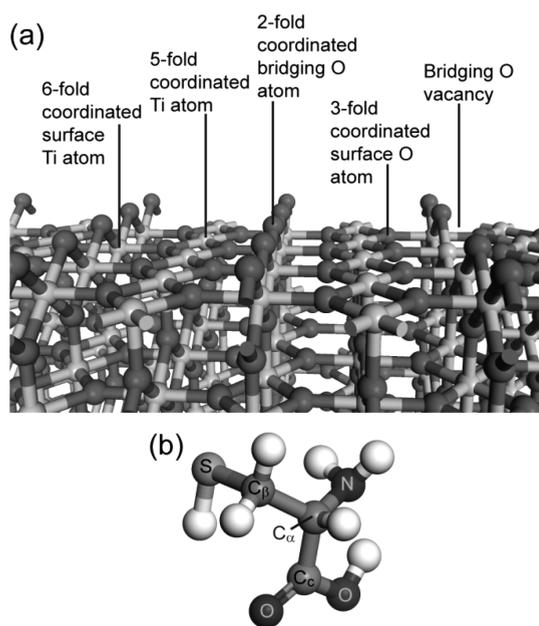
Figure 1. Ball and stick representations of the (a) rutile TiO$_2$(110) surface and (b) L-cysteine molecule. (a) Light and dark gray spheres represent Ti and O atoms, respectively, and important surface species are highlighted. (b) Atoms of the molecule are labeled, with the exception of the hydrogen atoms, which are represented by white spheres.

clusters. More specifically, we estimate that the gold clusters are by a factor two to three larger if gold is deposited first in comparison to when L-cysteine is preadsorbed on the surface.

2. EXPERIMENTAL SECTION

XPS measurements were performed at the soft X-ray beamline I511 of the National Swedish Synchrotron Radiation Facility MAX-lab in Lund. The spectroscopy end station of the beamline has separate preparation and analysis chambers. The preparation chamber contains an ion gun for surface sputtering, a mass spectrometer for residual gas analysis, and a low-energy electron diffraction (LEED) instrument. The analysis chamber is equipped with a Scienta R4000 electron energy analyzer for XPS measurements. The base pressure of both chambers is in the middle 10^{-10} mbar regime. The employed photon energy and total energy resolution are provided in the figures separately for each measurement. All spectra were calibrated to the Fermi level of the metal sample plate, which was in good ohmic contact with the TiO$_2$ crystal. Shirley-type backgrounds were removed from the S 2p and Au 4f spectra. For the C 1s spectra instead a fifth-order polynomial background was used to take into account the underlying Au NVV Auger signal. In the least-squares fits Voigt profiles were used.

L-Cysteine powder (99.5% pure) was purchased from Sigma-Aldrich and used without any further chemical purification. A home-built molecule evaporator, which consisted of a tantalum bag with a pinhole directed toward the crystal, was used to sublimate the molecules. The bag was heated by a direct electric current, and the temperature was measured using a type K thermocouple attached to the bag. The powder was degassed at 100−125 °C for about one-half a day before sublimation, and the molecules were then sublimated by heating the bag to various temperatures between 110 and 125 °C. During deposition the pressure in the preparation chamber increased by 1 order of magnitude. The L-cysteine coverage θ_{cys} was estimated by considering the intensity ratio of the substrate and molecular O 1s peaks (see ref 11 for details). A

full monolayer (1 ML$_{cys}$) of L-cysteine is achieved by adsorbing one molecule per two rutile TiO$_2$(110) surface unit cells; this is the densest packing of L-cysteine on the TiO$_2$(110) surface.[19]

Special care was taken to avoid X-ray beam damage to the sample. L-Cysteine degrades quite rapidly when exposed to X-rays. In order to prevent any influence on the spectra shown here the crystal was displaced continuously during the XPS measurements. The rate of beam damage was determined by exposing the nonmoving sample to the X-ray beam and identifying any beam-induced spectral changes by taking consecutive X-ray photoelectron spectra, each of which took around 20 s to measure. The sample displacement speed was then adjusted to ensure that no change was observed in the spectra. The total exposure time for any area on the sample was less than 100 s.

An EFM 3 metal evaporator (Omicron NanoTechnology GmbH, Germany) loaded with gold wire was used to deposit gold onto the TiO$_2$(110) surface. The evaporator was equipped with an internal fluxmeter. Flux × deposition time was used as a measure for the amount of gold sublimated. All gold coverages θ_{Au} are given in ML$_{Au}$, where 1 ML$_{Au}$ is the equivalent of a single atomic layer of the bulk-terminated Au(111) surface.[19] The gold coverages were obtained from measuring the full width at half-maximum (fwhm) of the Au 4f$_{7/2}$ peak measured on nonmodified Au/TiO$_2$(110) samples. In line with work by Howard et al.,[20] we assigned a full monolayer to the gold coverage at which the fwhm becomes constant, and all other gold coverages were determined relative to this specific coverage. Also, for the Au/L-cysteine/TiO$_2$(110) preparation the curves of coverage vs flux × deposition time obtained for the Au/TiO$_2$(110) sample were used for assigning coverages, and thus, it was assumed that the sticking coefficient is not affected by the presence of L-cysteine on the surface. Indeed, we found that the intensities in the raw Au 4f spectra were quite similar for the same nominal gold coverages, irrespective of deposition order, and hence, the assumption is at least roughly correct.
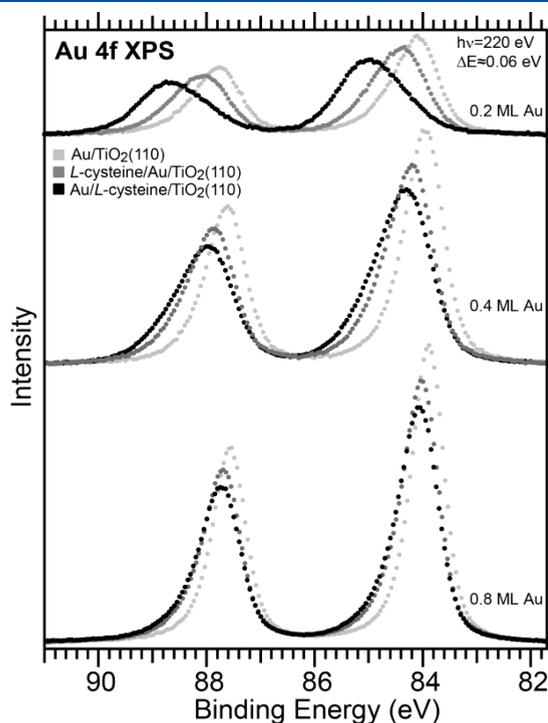
Rutile TiO$_2$(110) single crystals with dimensions $10 \times 10 \times 1$ mm^3 were purchased from PI-KEM, England, and mounted on a 1 mm thick molybdenum plate by molybdenum bolts and nuts. The sample was heated from the back side by a commercial boralectric heater (tectra GmbH, Germany), which provided homogeneous heating to the crystal. The temperature was measured using a type K thermocouple spot welded onto the sample plate close to the crystal. The TiO$_2$(110) crystal was cleaned by repeated cycles of sputtering by 1 keV Ar$^+$ ions for 15 min, followed by annealing at around 600 °C in UHV for 15 min, which resulted in a (1×1) LEED pattern.

3. RESULTS AND DISCUSSION

We investigated the deposition of gold clusters (gold coverages $\theta_{Au} = 0.2$, 0.4, and 0.8 ML$_{Au}$) on 0.5 ML$_{cys}$ L-cysteine preadsorbed on TiO$_2$(110) [Au/cysteine/TiO$_2$(110)] as well as the reverse deposition order of 0.5 ML$_{cys}$ L-cysteine adsorbed on predeposited gold clusters (same nominal coverages) on TiO$_2$-(110) [cysteine/Au/TiO$_2$(110)]. In section 3.1 we first focus on an analysis of the Au 4f X-ray photoelectron spectra with respect to the size of the Au clusters, which turns out to be different for the same gold coverages but reverse deposition orders of gold and L-cysteine. Then in section 3.2 we will discuss the interaction between the TiO$_2$(110) surface, L-cysteine, and gold clusters from a consideration of the S 2p, C 1s, O 1s, and N 1s X-ray photoelectron spectra.

3.1. Gold Cluster Size. The Au 4f XP spectra for all investigated coadsorption preparations of L-cysteine and gold as well as of pristine gold clusters on TiO$_2$(110) are shown in Figure 2 and the peak parameters in Table 1. The overall trend is that the Au 4f binding energies decrease with increasing gold cluster size toward the value for metallic gold and, likewise, that the full

width at half-maximum (fwhm) descreases with gold coverage; for each of the gold coverages the size of the binding energy shift is largest for the Au/L-cysteine/TiO$_2$(110) preparation and is smallest for the Au/TiO$_2$(110) sample. It is well known that smaller metal clusters exhibit larger binding energies and larger fwhms in photoemission spectra, i.e., the spectra are affected by a distinct cluster size effect (see, e.g., refs 20 and 21). Before we further pursue this cluster size issue, we note that part of the shift should rather be attributed to either a chemical shift or a changed core-hole screening response due to the interaction of L-cysteine with the gold clusters. We draw this conclusion since it seems reasonable to assume that the gold-cluster size is unchanged between the Au/TiO$_2$(110) and the L-cysteine/Au/TiO$_2$(110) preparations, and hence, the shifts observed for these samples cannot be explained by a cluster size effect. Indeed, adsorption of thiolates on gold surface has been found to induce thiolate-related components at higher Au 4f binding energy.[22,23] We also note that some peak broadening may be expected, since neither all surface atoms of the gold clusters (especially for the Au/L-cysteine/TiO$_2$(110) samples) nor the bulk atoms in the gold clusters will interact with the L-cysteine molecules. This will lead

to a stronger differentiation in chemical environment of the gold atoms and hence a broader peak, as observed.
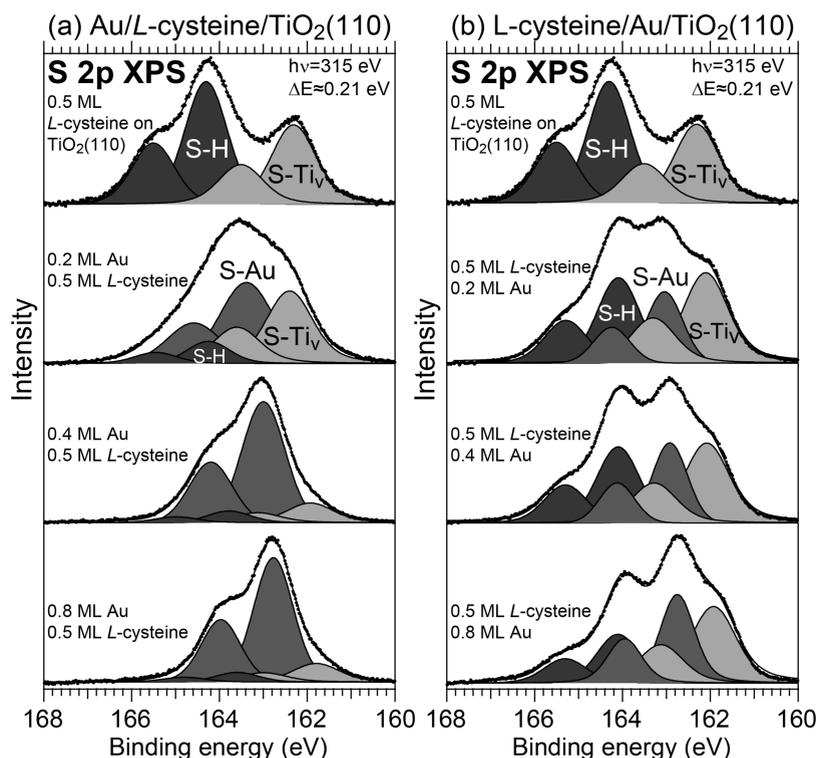
We now turn our attention again to the cluster size effect in the Au 4f spectra and evaluate it semiquantitatively according to the electrostatic model used in, e.g., refs 20, 24, and 25. In short, this model relates the binding energy shift and broadening of the photoemission line to the interaction of the positive charge left on the cluster in the photoemission process and the outgoing photoelectron. The model takes into account that the positive charge on the cluster has a limited lifetime and for TiO$_2$ that charge is provided to the cluster by the substrate on the low femtosecond time scale. The limited lifetime leads to the observation of a distribution of shifts, which can be calculated easily[20,25] and then convoluted with, e.g., a Gaussian to simulate the inherent line shape of the core level. A comparison with the shifts in the experimental spectra then allows an estimation of the cluster size.

For the pristine gold clusters on TiO$_2$(110) we find Au 4f$_{7/2}$ binding energy shifts of 0.2, 0.06, and 0 eV for coverages of 0.2, 0.4, and 0.8 ML$_{Au}$, respectively, measured relative to the value of the Au 4f$_{7/2}$ line for bulk metallic gold at 83.9 eV. Using the model described above—where the lifetime of the positive charge is assumed to be 1 fs—this corresponds to gold cluster radii of 23 Å (54 Å) for 0.2 ML$_{Au}$ (0.4 ML$_{Au}$).[26] Obviously, these values overestimate the cluster sizes, since gold clusters with radii of 25 Å have previously been found to have a metallic Au 4f$_{7/2}$ binding energy.[21,27] Accordingly, the clusters formed at θ_{Au}= 0.8 ML$_{Au}$ are expected to be found in this size range, but the clusters at θ_{Au}= 0.4 ML$_{Au}$ are not in disaccord with the predictions of the electrostatic model.

As already mentioned above, we assume that the clusters of the L-cysteine/Au/TiO$_2$(110) preparations have the same size as for Au/TiO$_2$(110). The binding energy shifts relative to the metallic value for Au/L-cysteine/TiO$_2$(110) are 1.05, 0.4, and 0.15 eV for ML$_{Au}$= 0.2, 0.4, and 0.8. From this we subtract the corresponding differences in binding energy shift found for the L-cysteine/Au/TiO$_2$(110) and Au/TiO$_2$(110) samples, which, as discussed above, we rather attribute to chemical shifts or changed screening due to the L-cysteine adsorption, and find shifts of 0.8, 0.16, and 0.04 eV, which should be interpreted in terms of the electrostatic model. From these shifts we find cluster radii of 8, 27, and 72 Å for 0.2, 0.4, and 0.8 ML$_{Au}$, respectively.

As already pointed out, the estimated cluster sizes are unrealistically large. Nevertheless, they give an idea of the right order of magnitude, and it is seen very clearly that the preadsorption of L-cysteine on TiO$_2$(110) leads to clusters, which are smaller by a factor of 2−3 than the corresponding gold clusters directly adsorbed on the TiO$_2$(110) surface.

3.2. Interaction of L-Cysteine with the TiO$_2$(110) Surface and Gold Clusters. *S 2p and C 1s X-ray Photoelectron Spectra.* S 2p X-ray photoelectron (XP) spectra are shown in Figure 3, both for the Au/L-cysteine/TiO$_2$(110) and for the L-cysteine/Au/TiO$_2$(110)

Figure 2. Au 4f spectra for three different adsorption conditions and three different gold coverages. Light gray, dark gray, and black curves show Au/TiO$_2$(110), L-cysteine/Au/TiO$_2$(110), and Au/L-cysteine/TiO$_2$(110) preparations, respectively. The spectra are normalized to the area of the Au/TiO$_2$(110) peak for each coverage.

Table 1. Au 4f$_{7/2}$ Parameters[a]

preparation	0.2 ML Au			0.4 ML Au			0.8 ML Au		
	BE	fwhm	ΔE	BE	fwhm	ΔE	BE	fwhm	ΔE
Au/TiO$_2$(110)	84.10	1.00	0	83.96	0.85	0	83.88	0.65	0
Au/L-cysteine/TiO$_2$(110)	84.95	1.50	0.85	84.30	1.30	0.34	84.05	0.90	0.17
L-cysteine/Au/TiO$_2$(110)	84.35	1.15	0.25	84.20	1.05	0.24	83.99	0.85	0.11

[a] All values are in eV. ΔE is the binding energy shift with respect to the Au/TiO$_2$(110) preparation.

Figure 3. S 2p XP spectra obtained on (a) gold deposited on top of L-cysteine/TiO$_2$(110) and (b) L-cysteine deposited on top of Au/TiO$_2$(110). The amounts of gold and L-cysteine are indicated for each spectrum. The spectra were normalized to the point of highest intensity. The components due to different sulfur species are coded always using the same gray tone: S—H, intact thiol groups; S—Au, thiolate interacting with gold clusters; S—Ti$_v$, thiolate interacting with surface defects. The solid lines are results of least-squares curve fitting. ΔE is the overall instrumental resolution.

Table 2. S 2p Least-Square Fit Parameters^a

|	S—H			S—Au			S—Ti$_v$		
preparation	BE	fwhm	intensity	BE	fwhm	intensity	BE	fwhm	intensity
0.5 ML L-cysteine/TiO$_2$(110)	164.31	1.14	58%				162.31	1.19	42%
0.2 ML Au/0.5 ML L-cysteine/TiO$_2$(110)	164.25	1.14	11%	163.38	1.42	48%	162.40	1.24	41%
0.4 ML Au/0.5 ML L-cysteine/TiO$_2$(110)	163.78	1.14	9%	163.00	1.15	71%	161.93	1.24	20%
0.8 ML Au/0.5 ML L-cysteine/TiO$_2$(110)	163.60	1.14	6%	162.77	1.05	79%	161.79	1.24	15%
0.5 ML L-cysteine/0.2 ML Au/TiO$_2$(110)	164.09	1.14	35%	163.04	0.97	23%	162.10	1.20	42%
0.5 ML L-cysteine/0.4 ML Au/TiO$_2$(110)	164.10	1.14	33%	162.92	0.93	27%	162.08	1.20	40%
0.5 ML L-cysteine/0.8 ML Au/TiO$_2$(110)	164.10	1.14	23%	162.75	0.92	36%	161.93	1.20	41%

^{a} Binding energies (BE) and full widths at half maximum (fwhm) are given in eV. The intensities are given as percentage of the overall intensity. The fwhms in italics were fixed at the given values in the fit. The uncertainty of the binding energies and fwhms is estimated to be 0.1–0.2 eV.

samples. The results from least-squares curve fitting are shown as solid lines with the individual components as shadowed peaks; the corresponding parameters are provided in Table 2. In the curve fit the energy difference between the S 2p$_{1/2}$ and the S 2p$_{3/2}$ components was fixed to 1.2 eV and the branching ratio to 1:2.[28] In the following all cited S 2p binding energies are those of the S 2p$_{3/2}$ components.

The spectrum obtained on the pure L-cysteine film in the absence of gold contains two components at binding energies of approximately 164.3 and 162.3 eV. In accordance with earlier work[11] these are assigned to thiol (S—H) and deprotonated thiol (S—Ti$_v$) groups, respectively. Previously, we suggested that deprotonated thiol groups are bound to 5-fold-coordinated Ti atoms formed at bridging oxygen vacancy sites (Ti$_v$), and thus,

the same assignment is made here. We note, though, that an interaction with titanium interstitials might produce the same kind of result, as mentioned in the Introduction.

Upon deposition of 0.2 ML$_{Au}$ gold on top of the L-cysteine film the S—H doublet is reduced significantly in intensity, and instead, a new doublet emerges at approximately 163.5 eV. The S—Ti$_v$ signal decreases slightly in intensity but remains quite unchanged otherwise. It is well known that the interaction of thiols with gold surfaces leads to deprotonation of the functional group and formation of a strong, covalent bond with the surface (see, e.g., ref 29). We therefore suggest that the new component is related to gold-coordinated thiolates, which we indicate by the label component "S—Au". The binding energy of this component is significantly higher, 1.5 eV, than what has been reported previously
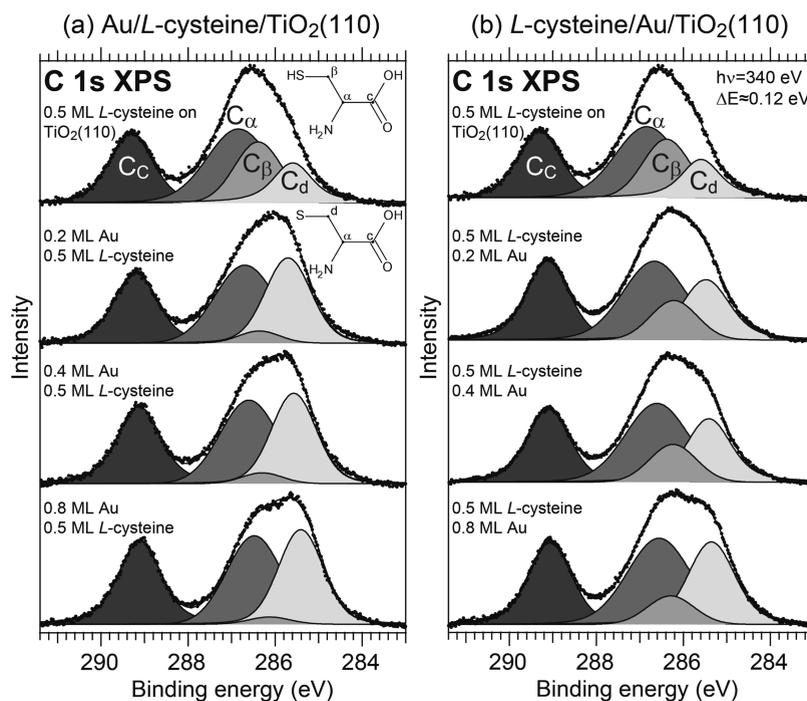
Figure 4. C 1s XP spectra for the following samples: (a) gold deposited on top of 0.5 ML L-cysteine on $TiO_2(110)$ surface and (b) 0.5 ML L-cysteine deposited on top of $Au/TiO_2(110)$. The amounts of gold and L-cysteine are given for each spectrum. The C_c, C_α, C_β, and C_d components are due to photoemission from the carboxylic carbon, amino-, thiol-, and thiolate-bonded carbon atoms, respectively [cf. the molecular structures of the intact molecule and thiolate depicted in panel a]. Least-square fits to the experimental data are depicted as lines. The spectra were normalized to the peak intensity; photon energy and overall instrumental resolution (ΔE) were the same for all measurements and are given in panel b.

for the L-cysteine thiolate on bulk gold surfaces (161.9 eV, ref 30; we found a S 2p binding energy of 162.0 eV for L-cysteine deposited on a very thick gold film grown on $TiO_2(110)$). The deviation from the literature value is seen to decrease to 0.75 eV for deposition of 0.8 ML_{Au} of gold. Probably this difference is related to the size of the gold clusters, which the L-cysteine molecules bind to, as compared to the bulk gold sample studied in the literature. Hence, the S–Au line is found to mirror the behavior of the Au 4f line, for which a similar—but smaller—shift to higher binding energies is found (cf. section 3.1). Presently, we cannot conclusively explain why the shift is larger by a factor of 2 (for 0.2 ML_{Au}) to 4 (for 0.8 ML_{Au}) in the S 2p than in the Au 4f line.

For increasing amounts of gold on L-cysteine/$TiO_2(110)$ the S–H peak is reduced further in intensity. This development is feasible and expected, since the deposited gold clusters will grow and eventually, for a very high coverage, would cover all L-cysteine molecules. The S–Au and S–Ti_v peaks shift to lower binding energies by approximately 0.6 eV, and the width of the S–Au peak decreases by around 0.35 eV. While the S–Ti_v peak is not reduced in intensity after deposition of θ_{Au} = 0.4 ML_{Au}, this is changed at the two highest gold coverages, θ_{Au} = 0.4 ML_{Au} and 0.8 ML_{Au}, for which not only the S–H species is converted into the S–Au-type of molecule but also an increasing share of the S–Ti_v species. Qualitatively, the spectral evolution shows that an interaction of gold with the S–H species is energetically more favorable than an interaction with the defect-bonded S–Ti_v species, since most of the S–H type of molecules are converted into S–Au before the S–Ti_v components starts to decrease in intensity. More quantitatively, we find from the deposited amounts of L-cysteine (θ_{cys}= 0.5

ML_{cys}) and gold that for preparation with θ_{Au}= 0.2 ML_{Au} approximately two gold atoms are available per L-cysteine molecule.[19] Only the L-cysteine species, which gives rise to the S–Au component of the S 2p spectra, binds to the gold clusters. The spectral intensity of this component is 48% of the total intensity (see Table 2), from which we conclude that, on average, there are 4 gold atoms available per L-cysteine molecule of S–Au type. This implies that once this average size of the gold clusters, which interact with the L-cysteine molecules, has reached approximately four gold atoms per molecule, it becomes energetically favorable to release the remaining L-cysteine molecules of S–Ti_v type from the defects and to instead form gold–thiolate bonds also to these molecules.

It is seen that the S–Ti_v component of the S 2p spectra does not vanish completely. We suggest that this might be related to L-cysteine species which are bonded to other defect sites than vacancies, such as step edges or Ti interstitials promoted to the surface. Alternatively, it is possible that roughly 35% of the vacancy-bonded thiolates survive the deposition of gold.

Figure 4a shows the C 1s spectra for the Au/L-cysteine/$TiO_2(110)$ preparations. The spectra were curve fitted with four components each, and the parameters are provided in Table 3. It should be noted that the very broad shape of the main peak renders the uncertainties of the parameters relatively large for the components fitted to this peak. Since the fits agree with the results obtained from the S 2p spectra (see the description in the following) we nevertheless think that they can serve to show the feasibility of our model.

The four components in the spectrum of the pristine L-cysteine layer are assigned to photoemission from the carboxylic carbon (C_c), amino group-bonded carbon (C_α), intact thiol

Table 3. C 1s Least-Square Fit Parameters[a]

preparation	C_c			C_α			C_β			C_d		
	BE	fwhm	area	BE	fwhm	area	BE	fwhm	area	BE	fwhm	area
0.5 ML L-cysteine/TiO$_2$(110)	289.31	1.18	26%	286.84	1.70	37%	286.39	1.27	22%	285.60	1.06	16%
0.2 ML Au/0.5 ML L-cysteine/TiO$_2$(110)	289.20	1.17	28%	286.69	1.62	36%	286.36	1.10	4%	285.70	1.17	32%
0.4 ML Au/0.5 ML L-cysteine/TiO$_2$(110)	289.13	1.17	30%	286.60	1.54	35%	286.30	*1.10*	3%	285.57	1.14	32%
0.8 ML Au/0.5 ML L-cysteine/TiO$_2$(110)	289.11	1.15	31%	286.48	1.47	35%	286.13	*1.10*	2%	285.41	1.14	32%
0.5 ML L-cysteine/0.2 ML Au/TiO$_2$(110)	289.13	1.17	27%	286.67	1.71	36%	286.22	1.27	13%	285.48	1.27	24%
0.5 ML L-cysteine/0.4 ML Au/TiO$_2$(110)	289.11	*1.17*	26%	286.61	*1.71*	37%	286.24	*1.27*	12%	285.41	1.20	25%
0.5 ML L-cysteine/0.8 ML Au/TiO$_2$(110)	289.07	*1.17*	26%	286.56	*1.71*	37%	286.29	*1.27*	8%	285.36	1.26	29%

[a] Binding energies (BE) and full widths at half maximum (fwhm) are given in eV. The intensities are given as a percentage of the overall intensity. In the curve fit the following constraints were applied: in agreement with the molecular stoichiometry, the summed intensity of the C_β + C_d peaks was set equal to the intensity of the C_α component, and the intensity ratio C_β/C_d was set equal to the corresponding S—H/(S—Ti$_v$ + S—Au) ratio in the S 2p spectra. fwhms in italics were held at the given values. The uncertainty of the binding energies and fwhms is estimated to be 0.1–0.2 eV.

group-bonded carbon (C_β), and dissociated thiol group-bonded carbon (C_d) carbon species.[11] In the curve fits the intensity ratios of the C_α, C_β, and C_d were constrained so that they agree with the S 2p results and the stoichiometry of L-cysteine, i.e.,

$$I_{C_\alpha} = I_{C_\beta} = I_{C_d}$$

$$\frac{I_{S-H}}{I_{S-Au} + I_{S-Ti_v}} = \frac{I_{C_\beta}}{I_{C_d}}$$

where the Is represent the spectral intensities. The intensity of the C_c component is slightly smaller than expected from the stoichiometry of the compound, which agrees with the notion of a support bond via the carboxylic group; in this geometry the photoelectrons from the carboxylic carbon atom will suffer stronger inelastic losses than those from the other molecular carbon atoms. The C_d type of carbon atom occurs both in vacancy-bonded and in gold-bonded thiolates (i.e., in the S—Ti$_v$ and S—Au L-cysteine species). Deposition of gold leads to a shift of the main peak at around 286 eV to lower energies. This we explain by a conversion of the S—H type of L-cysteine molecules into the S—Au type, as also suggested by the S 2p measurements; the C_β intensity is then converted into additional C_d intensity, while the C_α intensity is largely unaffected. The binding energy of the C_c components gets only slightly smaller after deposition of gold. Since it forms a covalent bond to the TiO$_2$ support the carboxylic group is not expected to bind to the gold clusters; hence, the binding energy of the C_c component constitutes an internal reference. Using this internal reference it is seen that the C_d atoms of the bridging oxygen-vacancy bonded thiolates in the pristine L-cysteine layer are not entirely equivalent to the C_d atoms of the gold-bonded thiolate (S—Au) species: For $\theta_{Au} = 0.2$ ML$_{Au}$ the binding energy of the C_d component relative to that of the C_c component is increased by 0.2 eV with respect to the gold-free sample. For larger amounts of gold it then decreases again, and for $\theta_{Au} = 0.8$ ML$_{Au}$ it is the same as for the pristine sample. Hence, this component does not follow the monotonous trend in the binding energies (both relative and absolute) of the other C 1s components or that of the S 2p binding energies. This suggests that it actually comprises two different components, namely, those of the carbon atoms bonded to the deprotonated thiol groups in the vacancy- and gold-bonded thiolates. The latter of these two is expected to increase with gold coverage at the expense of the former, and the nonmonotonous development of the fwhm suggests that this indeed is the case.

Now turning to the reverse deposition order, i.e., to L-cysteine deposited on top of Au/TiO$_2$(110), it is seen from Figure 3b that the S 2p spectra develop quite differently as compared to the above case of Au/L-cysteine/TiO$_2$(110). At all gold coverages L-cysteine species of S—H, S—Au, and S—Ti$_v$ type coexist and the S—Ti$_v$ component does not decrease in intensity at all (cf. Table 2). Further, it is observed that the S—Au peak is considerably narrower than for L-cysteine/Au/TiO$_2$(110) and that the S—H peak remains constant in energy, while both the S—Au and the S—Ti$_v$ shift down in energy by around 0.2–0.3 eV. The continued presence of the S—H adsorbate type is a consequence of the fact that the surface never is completely covered by gold; the three-dimensional growth mode of gold on reduced TiO$_2$(110) from quite low gold coverages onward,[31,32] with nucleation of the clusters at bridging oxygen vacancies, oxygen adatoms, and step edges,[18,33,34] further emphasizes this effect. Hence, at all studied gold coverages a significant fraction of the surface between the gold clusters is bare and available for binding of L-cysteine, although the fraction decreases with coverage. To the extent that they are not located next to a gold cluster, the L-cysteine molecules will have no sulfur—gold bond and be of either the S—H or the S—Ti$_v$ type. In addition, there probably exist L-cysteine molecules, which bind to the gold clusters but not to the TiO$_2$ surface, as well as a L-cysteine species at the brim of the gold clusters, which binds to both the TiO$_2$ surface and the gold clusters, similarly to what has been proposed for adsorption of bi-isonicotinic acid on gold-modified TiO$_2$(110).[35] These two species give rise to the S—Au component in the S 2p spectra.

In a static picture, that is, if the density of bridging oxygen vacancies is assumed to be constant over time and homogeneous over the entire surface, one would expect that the intensity of the S—Ti$_v$ component in the S 2p spectra should develop with gold coverage in the same way as that of the S—H component. The reason is that both the S—H and the S—Ti$_v$ species should occur only on the bare TiO$_2$ surface, and thus, the corresponding spectra intensities should scale in the same way with the amount of available bare surface. Instead, the S—Ti$_v$ intensity is constant with gold coverage. This means that a vacancy—thiolate bond is energetically more favorable than a vacancy—gold cluster bond. The finding seems to be in contrast to the finding reported above for Au/L-cysteine/TiO$_2$(110) that a thiolate—gold cluster bond becomes more stable than a thiolate—vacancy bond above a certain cluster size. Possibly, this disagreement is given rise to by

different growth modes of the gold clusters for the different deposition orders: as we discuss in detail below the (relatively small) gold clusters grow on top of the molecular layer for Au/L-cysteine/TiO$_2$(110) with the molecular layer remaining fixed in position, while for L-cysteine/Au/TiO$_2$(110) (larger) gold clusters are located directly on the TiO$_2$(110) surface, next to and possibly below the L-cysteine molecules. In the latter case a large fraction of the L-cysteine molecules is not in contact with any gold. If the gold clusters released the vacancies bonded beneath, the vacancies would get available for bonds to the non-gold-bonded L-cysteine molecules, and thereby the energy of the entire system would be lowered. A prerequisite for this model is that bigger gold clusters do not bind too strongly to the vacancies, in line with the previously observed tendency of lower adsorption energies for larger clusters on the reduced TiO$_2$(110) surface.[18] As a further parallel, we also would like to mention that it has been observed that water may displace—or partially displace and cobind with—gold atoms at the bridging oxygen vacancy sites.[36,37]

The C 1s spectra in Figure 4b (cf. the curve-fitting parameters in Table 3) confirm the picture just developed in the discussion of the S 2p spectra. The components in these C 1s spectra are assigned in the same way as for the Au/L-cysteine/TiO$_2$(110) preparations (note, again, that the uncertainties for the main peak components are relatively large). For L-cysteine/Au/TiO$_2$(110) the intensity of the C$_\beta$ component decreases with gold coverage and therefore gold cluster size at the benefit of the C$_d$ component attributed to L-cysteine molecules with a dissociated thiol group. The first gold deposition of 0.2 ML$_{Au}$ is found to lead to a rather rigid binding energy shift of 0.17–0.18 eV toward lower binding energy of all C 1s components, whose magnitude is comparable to the corresponding shifts of the S 2p components (0.21–0.22 eV); the only exception is the C$_d$ component, which shifts by only 0.12 eV. This deviation from the overall behavior can possibly be attributed to the dual nature of this component, which encompasses both vacancy- and gold-bonded thiolates. For the subsequent gold depositions only rather moderate binding energy shifts occur in the C 1s spectra.

O 1s and N 1s X-ray Photoelectron Spectra. It is also of interest to compare the evolution of the O 1s photoelectron spectra for the L-cysteine/Au/TiO$_2$(110) and Au/L-cysteine/TiO$_2$(110) preparations. The spectra are shown in Figure 5, and the corresponding curve-fit parameters are in Table 4. In accordance with what was found previously for L-cysteine adsorbed on TiO$_2$(110)[11] and other mono- and submonolayers of carboxylic acids on TiO$_2$(110) (see, e.g., refs 38–41), there exists only one molecular component in the spectra, which, not surprisingly, confirms that the two oxygen atoms of the carboxylic groups are equivalent and remain deprotonated. What is more interesting is how the relative intensity of the molecular peak develops with gold coverage in dependence on the deposition order. For L-cysteine/Au/TiO$_2$(110) it is seen to vary nonmonotonically, which possibly is related to photoelectron diffraction (for a particularly striking example of this effect, see ref 42), but overall it remains essentially constant for the different gold coverages. In contrast, for Au/L-cysteine/TiO$_2$(110) it decreases by roughly a factor of 2. This shows that in the latter case the gold clusters shadow the carboxylic groups and thus
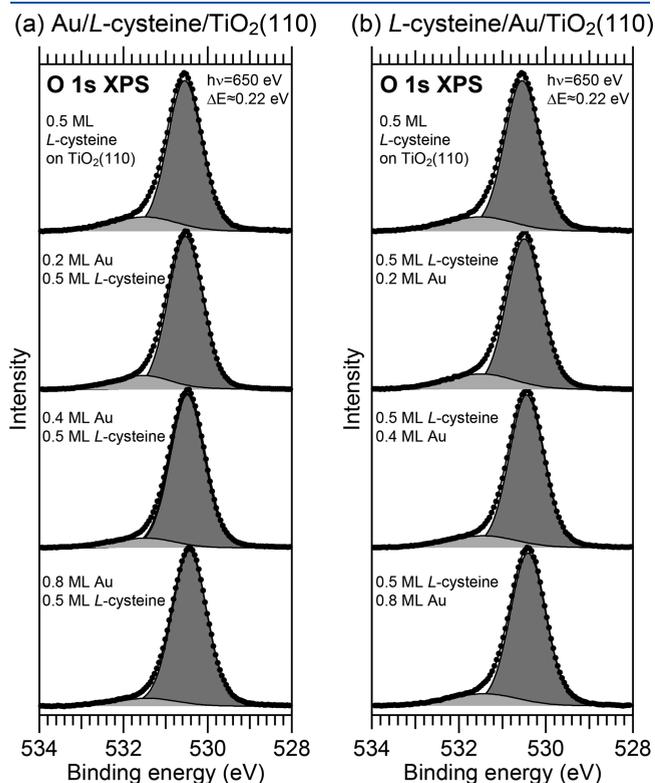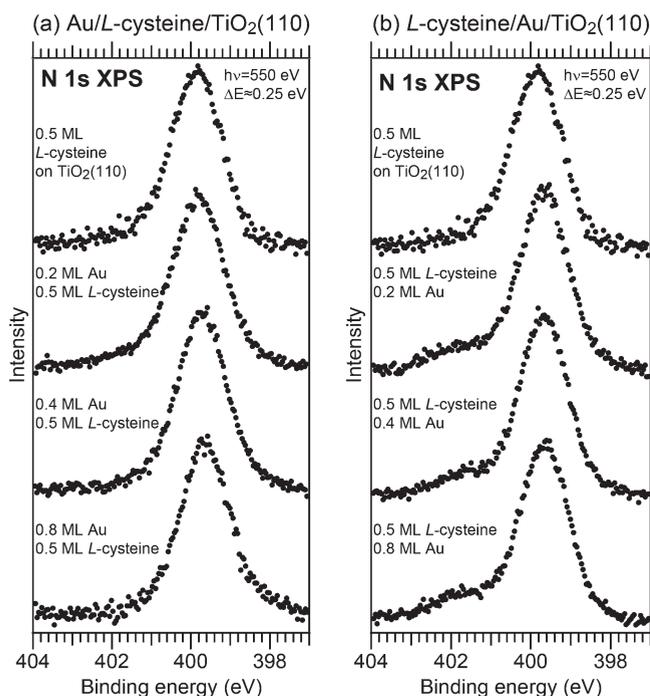

Figure 5. O 1s XP spectra. The curves were normalized to the height of the TiO$_2$ support component at low binding energy.

Table 4. O 1s Least-Square Fit Parameters[a]

preparation	COO$^-$			TiO$_2$		
	BE	fwhm	area	BE	fwhm	area
0.5 ML L-cysteine/TiO$_2$(110)	531.50	1.77	14%	530.54	0.97	86%
0.2 ML Au/0.5 ML L-cysteine/TiO$_2$(110)	531.53	1.52	14%	530.53	0.97	86%
0.4 ML Au/0.5 ML L-cysteine/TiO$_2$(110)	531.48	1.63	9%	530.48	0.97	91%
0.8 ML Au/0.5 ML L-cysteine/TiO$_2$(110)	531.43	1.65	8%	530.43	0.96	92%
0.5 ML L-cysteine/0.2 ML Au/TiO$_2$(110)	531.44	1.76	12%	530.44	0.89	88%
0.5 ML L-cysteine/0.4 ML Au/TiO$_2$(110)	531.49	1.80	15%	530.49	0.90	85%
0.5 ML L-cysteine/0.8 ML Au/TiO$_2$(110)	531.41	1.78	13%	530.31	0.88	87%

[a] Binding energies (BE) and full widths at half maximum (fwhm) are given in eV. The intensities are given as a percentage of the overall intensity. The difference in binding energy between the substrate and the molecular peaks was set to 1 eV in agreement with previous work.[11] The uncertainty of the binding energies and fwhms is estimated to be 0.1–0.2 eV.

(a) Au/L-cysteine/TiO$_2$(110)

N 1s XPS   hν=550 eV
ΔE≈0.25 eV

0.5 ML
L-cysteine
on TiO$_2$(110)

0.2 ML Au
0.5 ML L-cysteine

0.4 ML Au
0.5 ML L-cysteine

0.8 ML Au
0.5 ML L-cysteine

Intensity

404   402   400   398
Binding energy (eV)

(b) L-cysteine/Au/TiO$_2$(110)

N 1s XPS   hν=550 eV
ΔE≈0.25 eV

0.5 ML
L-cysteine
on TiO$_2$(110)

0.5 ML L-cysteine
0.2 ML Au

0.5 ML L-cysteine
0.4 ML Au

0.5 ML L-cysteine
0.8 ML Au

Intensity

404   402   400   398
Binding energy (eV)

Figure 6. N 1s XP spectra. The curves were normalized to the height of the most intense component. The peak positions are as follows: 399.8 eV for the pristine L-cysteine layer on TiO$_2$(110); 399.8, 399.7, and 399.6 eV for 0.2, 0.4, and 0.8 ML$_{Au}$ adsorbed on L-cysteine on TiO$_2$-(110); 399.8, 399.65, 399.65, and 399.65 eV for 0.5 ML$_{cys}$ L-cysteine adsorbed on 0.2, 0.4, and 0.8 ML$_{Au}$ on TiO$_2$(110).

grow on the molecular layer. Since the clusters already have a considerable size at all studied gold coverages (see below) and in view of the fact that the coverage of L-cysteine is only $\theta_{cys} = 0.5$, it is possible, however, that they also are in direct contact with the TiO$_2$ surface.[43]

In the N 1s X-ray photoelectron spectra in Figure 6 another difference is found between the Au/L-cysteine/TiO$_2$(110) and the L-cysteine/Au/TiO$_2$(110) preparations. For the Au/L-cysteine/TiO$_2$(110) samples the N 1s line of the pristine L-cysteine layer and those with gold added are virtually identical, apart from an overall shift to lower binding energy, which increases with gold coverage. In contrast, for the L-cysteine/Au/TiO$_2$(110) preparations the main peaks are all found at the same binding energy, which is lower than that of the pristine L-cysteine layer and identical to that found for the high gold coverage Au/L-cysteine/TiO$_2$(110) preparation. Furthermore, a component at higher binding energy appears in the spectra. It is alluring to assign this component to NH$_3^+$ groups, since the shift (around 2 eV) is quite identical to what we assigned to protonated amino groups occurring in the L-cysteine//TiO$_2$(110) sample at higher L-cysteine coverages not investigated here[11] and what was found for L-cysteine adsorbed on gold.[30,44] Possibly, the observation of the high-binding energy component is related to adsorption of L-cysteine on the gold clusters. It is noted, though, that NH$_2$—Au interactions are favorable[45−47] and also may induce a shift of the N 1s signal to higher XPS binding energies.[48]

4. SUMMARY AND CONCLUSIONS

We investigated the coadsorption of gold and L-cysteine on a TiO$_2$(110) surface and studied both the adsorption of gold on an

L-cysteine layer on TiO$_2$(110) and the adsorption of L-cysteine on gold clusters supported by the TiO$_2$(110) surface. For deposition of gold on top of a preformed L-cysteine layer we find that the gold clusters tend to grow on top of the molecular layer. The interaction leads to a dissociation of the thiol groups of the L-cysteine molecules and formation of a gold—thiolate bond. The cluster size remains by a factor of 2−3 smaller in comparison to that of gold clusters formed when the same amount of gold is deposited directly onto the clean TiO$_2$(110) surface. Apart from deprotonation of the thiol group, concomitant with the binding of the thiolates to the gold clusters, the geometry and chemistry of the L-cysteine layer are not affected substantially, i.e., the support—molecule bond via the carboxylic group remains intact and the amino groups are not involved in any interaction. When L-cysteine is adsorbed onto gold clusters on TiO$_2$(110) we find a molecular species, which does not interact with the gold clusters. In addition, we observe molecular species, which do interact with the metal clusters via their thiol groups. Finally, in preparations of L-cysteine deposited on Au/TiO$_2$(110) L-cysteine can displace the gold clusters from the bridging oxygen vacancies. We conclude that the L-cysteine—vacancy bond is stronger than the gold cluster—vacancy bond. In turn, we found spectral evidence that if the average size of the gold clusters reaches approximately four atoms which are deposited on top of L-cysteine/TiO$_2$(110), L-cysteine prefers to bind to the gold clusters rather than the bridging oxygen vacancies. From this we conclude that the interaction between the gold clusters and L-cysteine is stronger than that between L-cysteine and the bridging oxygen vacancies of the surface. Altogether, we find that the L-cysteine—gold bond is stronger than the L-cysteine—vacancy bond, which, in turn, is stronger than the gold cluster—vacancy bond.

An aspect which remains somewhat unclear is the size of the observed binding energy shifts in the S 2p line. The shifts seem to follow the shifts seen in the Au 4f line and are thus at least partially related to the size of the gold clusters. However, the magnitude of the S 2p shifts is larger than that of the Au 4f shifts, as well as that observed in the C 1s, O 1s, and N 1s spectra. While band bending may play some role, the resulting shifts should be approximately the same for the different core levels. Hence, another factor must play in, and this can only be the exact binding mode of the L-cysteine molecules in the different preparations. A clarification of this point will have to await further experimental and theoretical efforts.

The results demonstrate that modification of a TiO$_2$ surface or any other oxide surface by a properly chosen thiol can assist in tailoring the size of deposited gold particles. Thus far we have not, however, investigated whether the gold particles bonded to the thiols retain, or can regain, any functionality in terms of their catalytic activity. Future work will also have to clarify how exposure to a reactive atmosphere and perhaps even warming affect the metal—organic structure at the TiO$_2$ surface.

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■ REFERENCES

(1) Hammer, B.; Nørskov, J. K. Nature 1995, 376, 238.

(2) Haruta, M. Catal. Today 1997, 36, 153.

(3) Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama, H.; Genet, M. J.; Delmon, B. J. Catal. 1993, 144, 175.

(4) Valden, M.; Lai, X.; Goodman, D. W. Science 1998, 281, 1647.

(5) Yang, F.; Chen, M. S.; Goodman, D. W. J. Phys. Chem. C 2009, 113, 254.

(6) Cao, A.; Lu, R.; Veser, G. Phys. Chem. Chem. Phys. 2010, 12, 13499.

(7) Lopez-Acevedo, O.; Kacprzak, K. A.; Akola, J.; Häkkinen, H. Nat. Chem. 2010, 2, 329.

(8) Daniel, M. -C.; Astruc, D. Chem. Rev. 2004, 104, 293.

(9) Zhu, Y.; Qian, H.; Zhu, M.; Jin, R. Adv. Mater. 2010, 22, 1915.

(10) Zhu, Y.; Qian, H.; Jin, R. Chem. Eur. J. 2010, 16, 11455.

(11) Ataman, E.; Isvoranu, C.; Knudsen, J.; Schulte, K.; Andersen, J. N.; Schnadt, J. Surf. Sci. 2011, 605, 179.

(12) Wendt, S.; Sprunger, P. T.; Lira, E.; Madsen, G. K. H.; Li, Z.; Hansen, J. Ø.; Matthiesen, J.; Blekinge-Rasmussen, M.; Lægsgaard, E.; Hammer, B.; Besenbacher, F. Science 2008, 320, 1755.

(13) Yim, C. M.; Pang, C. L.; Thornton, G. Phys. Rev. Lett. 2010, 104, 036806.

(14) Wendt, S.; Bechstein, R.; Porsgaard, S.; Lira, E.; Hansen, J. Ø.; Huo, P.; Li, Z.; Hammer, B.; Besenbacher, F. Phys. Rev. Lett. 2010, 104, 259703.

(15) Yim, C. M.; Pang, C. L.; Thornton, G. Phys. Rev. Lett. 2010, 104, 259704.

(16) Madsen, G. K. H.; Hammer, B. J. Chem. Phys. 2009, 130, 044704.

(17) Stausholm-Møller, J.; Kristoffersen, H. H.; Hinnemann, B.; Madsen, G. K. H.; Hammer, B. J. Chem. Phys. 2010, 133, 144708.

(18) Matthey, D.; Wang, J. G.; Wendt, S.; Matthiesen, J.; Schaub, R.; Lægsgaard, E.; Hammer, B.; Besenbacher, F. Science 2007, 315, 1692.

(19) Since the definitions of one monolayer are different for the gold and L-cysteine coverages, we distinguish them by using "ML_{Au}" and "ML_{cys}" as monolayer units. One ML_{Au} corresponds to 1.39×10^{15} atoms/cm^2 and, since at full monolayer coverage one L-cysteine molecule occupies two TiO$_2$(110) unit cells, each with a size of 19.21 Å^2, 1 ML_{cys} to 2.6×10^{14} molecules/cm^2.

(20) Howard, A.; Clark, D. N. S.; Mitchell, C. E. J.; Egdell, R. G.; Dhanak, V. R. Surf. Sci. 2002, 518, 210.

(21) Kitsudo, Y.; Iwamoto, A.; Matsumoto, H.; Mitsuhara, K.; Nishimura, T.; Takizawa, M.; Akita, T.; Maeda, Y.; Kido, Y. Surf. Sci. 2009, 603, 2108.

(22) Chaudhuri, A.; Lerotholi, T. J.; Jackson, D. C.; Woodruff, D. P.; Dhanak, V. Phys. Rev. Lett. 2009, 102, 126101.

(23) Tanaka, A.; Imamura, M.; Yasuda, H. Phys. Rev. B 2006, 74, 113402.

(24) Wertheim, G. K.; DiCenzo, S. B.; Youngquist, S. E. Phys. Rev. Lett. 1983, 51, 2310.

(25) Hövel, H.; Grimm, B.; Pollmann, M.; Reihl, B. Phys. Rev. Lett. 1998, 81, 4608.

(26) We assumed that α = 0.5, where αe is the effective charge left behind on the cluster, i.e., α describes the immediate screening of the core hole provided by the cluster itself. Further, we assumed that the inherent line shape of the Au 4f$_{7/2}$ photoemission line is Gaussian with a full width at half-maximum (fwhm) of 1 eV. While this is not particularly realistic, we found that a reduction of the fwhm did not change the resulting cluster sizes by more than 0.1 Å.

(27) Lim, D. C.; Lopez-Salido, I.; Dietsche, R.; Bubek, M.; Kim, Y. D. Surf. Sci. 2006, 600, 507.

(28) Svensson, S.; Naves de Brito, A.; Keane, M. P.; Correia, N.; Karlsson, L. Phys. Rev. A 1991, 43, 6441.

(29) Dubois, L. H.; Nuzzo, R. G. Annu. Rev. Phys. Chem. 1992, 43, 437.

(30) Cavalleri, O.; Gonella, G.; Terreni, S.; Vignolo, M.; Floreano, L.; Morgante, A.; Canepa, M; Rolandi, R. Phys. Chem. Chem. Phys. 2004, 6, 4042.

(31) Parker, S. C.; Campbell, C. T. Top. Catal. 2007, 44, 3.

(32) Cosandey, F.; Madey, T. E. Surf. Rev. Lett. 2001, 8, 73.

(33) Minato, T.; Suaski, T.; Shiraki, S.; Kato, H. S.; Kawai, M.; Aika, K. Surf. Sci. 2004, 566−568, 1012.

(34) Wahlström, E.; Lopez, N.; Schaub, R.; Thostrup, P.; Rønnau, A.; Africh, C.; Lægsgaard, E.; Nørskov, J. K.; Besenbacher, F. Phys. Rev. Lett. 2003, 90, 026101.

(35) Taylor, J. B.; Mayor, L. C.; Swarbrick, J. C.; O'Shea, J. N.; Schnadt, J. J. Phys. Chem. C 2007, 111, 16646.

(36) Tong, X.; Benz, L.; Chrétien, S.; Metiu, H.; Bowers, M. T.; Buratto, S. K. J. Phys. Chem. C 2010, 114, 3987.

(37) Wu, T.; Kaden, W. E.; Anderson, S. L. J. Phys. Chem. C 2008, 112, 9006.

(38) Guo, Q.; Cocks, I.; Williams, E. M. Surf. Sci. 1997, 393, 1.

(39) Chambers, S. A.; Henderson, M. A.; Kim, Y. J.; Thevuthasan, S. Surf. Rev. Lett. 1998, 5, 381.

(40) Patthey, L.; Rensmo, H.; Persson, P.; Westermark, K.; Vayssieres, L.; Stashans, A.; Petersson, Å.; Brühwiler, P. A.; Siegbahn, H.; Lunell, S.; Mårtensson, N. J. Chem. Phys. 1999, 110, 5913.

(41) Schnadt, J.; O'Shea, J. N.; Patthey, L.; Schiessling, J.; Krempaský, J.; Shi, M.; Mårtensson, N.; Brühwiler, P. A. Surf. Sci. 2003, 544, 74.

(42) Wiklund, M.; Beutler, A.; Nyholm, R.; Andersen, J. N. Surf. Sci. 2000, 461, 107.

(43) Thermal desorption of L-cysteine as a result of gold deposition is not considered, since the adsorption energies of carboxylates on TiO$_2$(110) and L-cysteine on gold are too high to allow for thermal desorption at room temperature.

(44) Gonella, G.; Terreni, S.; Cvetko, D.; Cossaro, A.; Mattera, L.; Cavalleri, O.; Rolandi, R.; Morgante, A.; Floreano, L.; Canepa, C. J. Phys. Chem. B 2005, 109, 18003.

(45) Hoft, R. C; Ford, M. J.; McDonagh, A. M.; Cortie, M. B. J. Phys. Chem. C 2007, 111, 13886.

(46) Höffling, B.; Ortmann, F.; Hannewald, K.; Bechstedt, F. Phys. Status Solidi C 2010, 7, 149.

(47) Michota, A.; Kudelski, A.; Bukowska, J. Surf. Sci. 2002, 502−503, 214.

(48) Cossaro, A.; Dell'Angela, M.; Verdini, A.; Puppin, M.; Kaldnik, G.; Coreno, M.; Kivimäki, A.; Cvetko, D.; Canepa, M.; Floreano, L. J. Phys. Chem. C 2010, 114, 15011.