

Molecular Understanding of Reactivity and Selectivity for Methanol Oxidation at the Au/TiO₂ Interface**

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Gold-based catalysts have attracted great interest since the discovery of the exceptional catalytic activity of oxide-supported Au nanoparticles for a large number of oxidation reactions including low-temperature CO oxidation.^[1] Despite extensive experimental and theoretical studies,^[2–10] however, the origin of the high catalytic activity of Au/oxide catalysts has not been clarified. Many important issues such as the nature of the active sites and the activation of molecular oxygen are still under debate. In particular, little is known about the microscopic mechanism of complex reactions such as the selective oxidation of alcohol molecules on oxide-supported Au nanoparticles.^[11]

Methanol (CH₃OH) is one of the most important industrial chemicals^[12] and the selective oxidation of alcohols with oxygen is a key issue for the production of fine and specialty chemicals using “green” processes.^[13] Herein, we present a surface-science study of the selective oxidation of methanol on a Au/TiO₂(110) model catalyst. The combined data, obtained from extensive density functional theory (DFT) calculations and experiments using high-resolution electron energy loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS), allow us to achieve an atomic-level understanding of the low-temperature oxidation of methanol with molecular oxygen to formaldehyde. We demonstrate herein that the high catalytic activity and selectivity of Au/TiO₂ originate from the presence of active interfacial sites, where the activation of molecular oxygen

occurs through charge transfer from Au/TiO₂ forming O₂^{δ−} species. Oxygen activation is followed by the formation of a CH₃OH–O₂ intermediate, which undergoes oxidative dehydrogenation yielding CH₂O and H₂O. The latter is produced by recombination of hydroxy groups including hydrogen transfer from the Au cluster to an O atom at the perimeter site.

We first investigated the molecular reaction mechanism of the selective oxidation cycle of CH₃OH by O₂ on an Au₁₁/TiO₂(110) model surface by means of GGA + U calculations. It has been reported that very small unsupported and oxide-supported Au clusters (3–10 atoms) also show high catalytic activity towards CO oxidation and various organic reactions.^[14] We have studied in detail the electronic structure of a set of Au_n clusters (*n* = 11–16) supported on TiO₂(110) (see Supporting Information, Section III.H). It was demonstrated that the charge of the activated O₂^{δ−} species is almost constant (Table S3), indicating that the behavior of Au_n nanoclusters of different size, shape, and morphology is qualitatively the same with respect to O₂ activation. Therefore, the Au₁₁ model, although certainly being a simplification of nanometer-sized clusters on TiO₂(110), was shown to appropriately mimic the active sites located at the nanogold/oxide interface where the oxidation process takes place.^[15]

As shown in Figure 1 A, a Au₁₁ gold cluster was anchored at a single surface oxygen vacancy on the TiO₂(110) surface. Oxygen vacancies, which are always present on the rutile surface,^[16] result in stable anchoring sites for Au adatoms. In the case of an isolated oxygen vacancy on the stoichiometric TiO₂(110) surface, the charge neutrality is maintained by the presence of two Ti³⁺ ions.^[17] The stable binding of the Au₁₁ cluster on an oxygen vacancy site entails a strong charge rearrangement at the gold/oxide contact (central panel in Figure 1). The bonding charge analysis reveals that charge transfer occurs from the Au₁₁ cluster to the reduced oxide surface, thus leaving a reduced surface with three Ti³⁺ ions and a positively charged Au₁₁^{δ+} cluster.^[18] This finding is further supported by the HREELS data as discussed below (see also Figure S1).

All the steps involved in the proposed mechanism for CH₃OH oxidation at the active Au₁₁/TiO₂(110) interface are depicted in Figure 1; all underlying data are compiled in the Supporting Information including connecting pathways and much additional analyses (Figure S3–S14). The catalytic cycle starts with the adsorption of an O₂ molecule at the interface on a dual perimeter site between the Au₁₁ cluster and the TiO₂(110) surface (Figure 1 B) with a strong binding energy of −2.15 eV. The adsorbed O₂ molecule has an O–O bond length of 1.44 Å, close to the typical value for a peroxide (O₂^{2−}:

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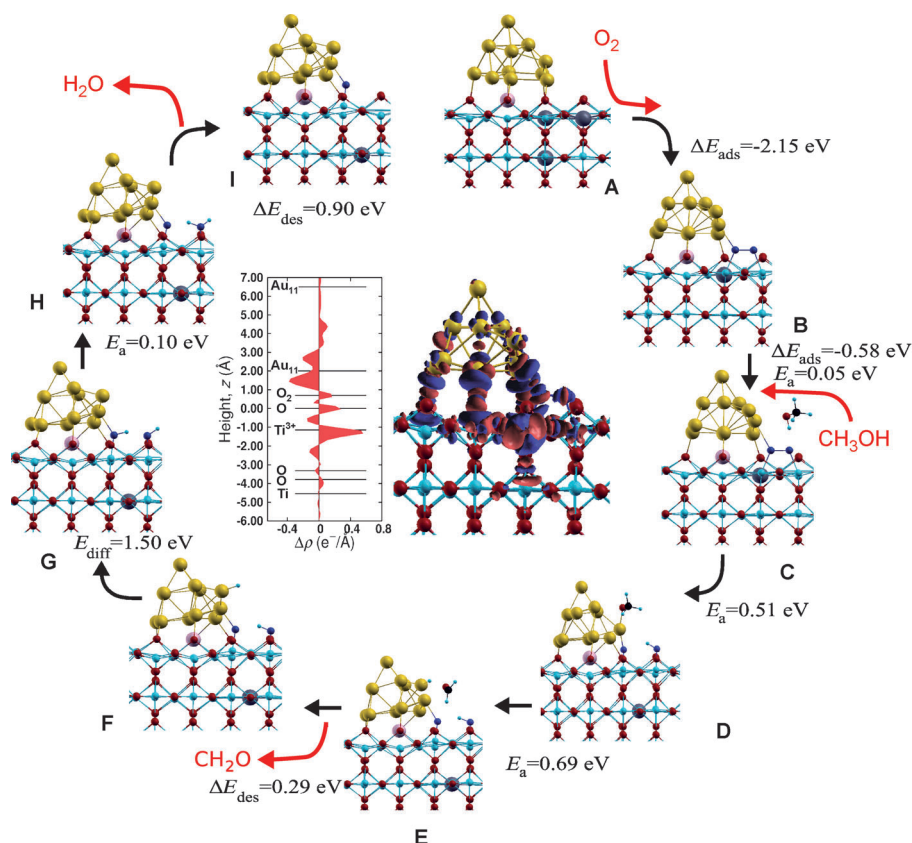


Figure 1. Selective methanol oxidation cycle proposed from calculations. The Au, Ti, O, and C atoms are shown in yellow, light blue, red, and black respectively, whereas the O₂ molecule adsorbed at the interface and H atoms of the CH₃OH molecule are shown in blue and small light blue spheres. The pink sphere represents the oxygen vacancy and the large dark spheres of the substrate show Ti³⁺ sites. ΔE_{ads} , E_a , ΔE_{des} , and E_{diff} refer to the adsorption energy, activation barrier, desorption energy, and diffusion barrier, respectively. The center of the Figure shows the calculated bonding charge $\Delta\rho$ for the Au₁₁ cluster supported by the reduced TiO₂(110) surface in the presence of a preadsorbed O₂ molecule. Left: the bonding charge integrated in planes perpendicular to the surface and is plotted as a function of the height from the surface. Right: the bonding charge plotted at the value of 0.06 |e| Å⁻³. Electron accumulation and depletion are represented by red and blue isosurfaces, respectively. Full details are provided in the Supporting Information.

1.49 Å). Each O atom binds to one surface Ti_{5c} atom. A close examination of the spin density, projected density of states (PDOS) and bonding charge reveals that upon O₂ adsorption the substrate degree of reduction changes: two of the three excess electrons originally populating Ti³⁺ sites of the titania surface are donated to the adsorbed O₂ molecule, which turns out to be a peroxide, while only one Ti³⁺ ion is present on the oxide support (see central panel in Figure 1). We note that the full catalytic cycle does not modify the degree of reduction of the oxide support, which indicates the presence of a single Ti³⁺ ion from the initial to the final state (Figure 1) of the proposed oxidation mechanism. This step is followed by the coadsorption of CH₃OH at the dual perimeter site on top of the O₂/TiO₂(110) (Figure 1C) with a binding energy of -0.58 eV. The adsorbed CH₃OH reacts directly with O₂/TiO₂(110) to form a CH₃OH-O₂ intermediate that is stabilized by interaction with the neighboring Au site right at the interface. As a result the O-O bond is weakened upon its interaction with CH₃OH, and dissociates with an activation

energy of 0.05 eV to form Ti_{5c}-OH and Au-CH₃O (Figure 1D). This step involves the rupture of the O-O bond of the preadsorbed O₂ molecule, an H atom transfer from the methanol OH group to the surface O atom, and the binding of methoxy (CH₃O) to the neighboring Au atom (Figure S9). The O atom at the interface moves in the direction of the metal cluster, and the Au₁₁ cluster rearranges its shape with an activation energy of 0.51 eV. A close examination of the PDOS along the reaction path reveals that the dissociation of the perimeter molecule is accompanied by a significant charge transfer (approximately 0.6 valence electrons) from the Au₁₁ cluster to the dissociated O₂ molecule that stabilizes the Au-CH₃O intermediate (Figure S10).

The catalytic cycle proceeds through the formation of CH₂O from CH₃O by way of an additional oxidation. The calculated reaction path for the second oxidation step involves the donation of an H atom of the formed Au-CH₃O intermediate complex to a Au atom of the metal cluster. This step has an activation energy of 0.69 eV (Figure 1E). The supported Au₁₁ metal cluster accepts an H atom from CH₃O, therefore acting as a hydrogen storage device. The formed CH₂O can easily desorb with a desorption energy of 0.29 eV (Figure 1F). The last part of the cata-

lytic cycle concerns the formation of water. The H atom migrates on the gold cluster with a barrier of approximately 1.5 eV until it finds the activated O atom at the perimeter site to form an OH intermediate (Figure 1G), thereby changing its charge from close to 1.0 to about 0.5 |e|, i.e., transmuting from a H atom to a proton (Figure S13).

The hydroxy species thus formed can readily react with the neighboring OH group transferring the H atom with an activation energy of 0.10 eV, thereby leading to the formation of a H₂O molecule (Figure 1H). This H₂O molecule can desorb with a desorption energy of 0.90 eV (Figure 1I) thus completing the cycle and leaving behind an active O atom species at the interface. This step returns the catalyst surface to its initial working state, and the oxidation reaction can continue by adsorbing a second CH₃OH molecule at the Au perimeter site.

To examine the above microscopic mechanism for the high reactivity and selectivity of the Au/TiO₂ interface towards CH₃OH oxidation, we have carried out correspond-

ing experiments by means of HREELS and TDS. Following a method from the literature,^[19] the supported Au nano-clusters were prepared by evaporating Au at 300 K onto an vacuum-annealed TiO₂(110) surface, which exposes approximately 10% of the surface oxygen vacancies.^[20] The as-prepared sample was subsequently annealed at 750 K in vacuum to stabilize the Au clusters. The growth of Au clusters on rutile TiO₂(110) surfaces has been extensively studied by STM and non-contact AFM.^[19] Table S1 shows the average size, height, and density of Au clusters on TiO₂(110) as a function of the Au coverage reported in previous studies.^[2,19] After deposition of 0.2 monolayer (ML) Au on the reduced TiO₂(110) surface, the EELS spectrum shows a loss peak centered at 2.5 eV (Figure S1), which was assigned to the surface plasmon excitation of Au clusters.^[21] This band was not detected at Au coverage less than 0.2 ML, indicating that the structural transition of Au adatoms from 2D to 3D configurations occurs at around 0.2 ML.^[21] The loss at 0.8 eV originates from the excitation of shallow band gap states associated with Ti³⁺ sites at oxygen vacancies.^[22] Its intensity increases at the initial deposition of Au (up to 0.2 ML) implying the formation of additional Ti³⁺ ions through charge transfer from Au to TiO₂ substrates as confirmed by the DFT calculations (Figure 1 A). This band diminishes with further increasing Au coverage revealing that the Ti³⁺-related excitation is significantly screened owing to the growth of 3D Au clusters at oxygen vacancy sites (Figure 1 A).

The activation of molecular O₂ is a key issue for the low-temperature methanol oxidation on Au/TiO₂(110) and was studied by HREELS using CO exclusively as a probe molecule, which is extremely sensitive to the oxidation state of the Au species.^[23] The raw spectrum of Au/TiO₂(110) is dominated by intense fundamental (358, 437, and 743 cm⁻¹) and multiple surface phonons (Figure 2 A). The multiphonon-related losses have been successfully removed by Fourier

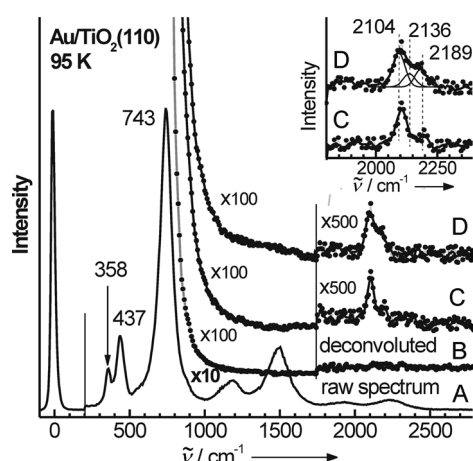


Figure 2. HREEL spectra of Au/TiO₂(110) obtained after CO adsorption at 95 K with and without O₂ preadsorption; note that CO is exclusively used as a probe molecule and not oxidized. A) The raw spectrum of clean Au/TiO₂ (0.4 ML Au). B) The spectrum obtained for clean Au/TiO₂ after Fourier deconvolution to remove the intense multiple surface phonons, C) deconvoluted spectrum for CO adsorption on Au/TiO₂ at 95 K, and D) deconvoluted spectrum for CO adsorption subsequent to O₂ adsorption on Au/TiO₂ at 95 K.

deconvolution (Figure 2B), which allows us to reliably identify adsorbate-induced energy losses. In the absence of O₂ preadsorption, CO adsorption on Au/TiO₂(110) (0.4 ML Au) at 95 K exhibits two stretching bands at 2104 cm⁻¹ and 2189 cm⁻¹ (Figure 2C). The latter one is assigned to CO bound to coordinatively unsaturated Ti⁴⁺ sites on the “free” TiO₂(110) surface,^[20] while the low-lying band at 2104 cm⁻¹ is characteristic of the CO species bound to undercoordinated neutral Au sites at the Au/TiO₂ interface.^[10,24] When the Au/TiO₂(110) sample is first exposed to O₂ and then to CO at 95 K, a new band emerges at 2136 cm⁻¹, indicating CO adsorption on the positively charged Au sites (Figure 2D). This band is further attributed to CO chemisorbed on low-coordinated Au sites in the presence of activated O₂ molecules at the interface, forming peroxy/superoxo-type O₂^{δ-}-Au^{δ+}-CO species.^[24] The blue-shift in frequency compared to the 2104 cm⁻¹ band originates from a charge transfer from Au/TiO₂ to molecular oxygen, which subsequently decreases the electron back-donation from Au to the CO 2π* antibonding orbital and thus strengthens the internal C–O bond. The HREELS data reveal that O₂ activation occurs at the Au/TiO₂ interface by way of charge transfer yielding an O₂^{δ-} species, whereas no direct dissociation to atomic oxygen was detected at low temperatures, in excellent agreement with the calculated data (Figure 1B; Figure S3).

The TDS results provide direct evidence for the selective oxidation of CH₃OH on Au/TiO₂(110). For all the TDS experiments, the heating temperature was limited below 730 K, at which Au cluster sintering does not occur,^[19] as confirmed by the reproducibility of the TD spectra. The corresponding TD spectra for CH₃OH, CH₂O, and H₂O are presented in Figure 3A–C. The TDS data reveal the occurrence of a well-known high-temperature reaction channel (> 600 K) forming CH₂O for both pure and Au-decorated TiO₂(110) surfaces (Figure 3B,D). The production of CH₂O is accompanied by CH₃OH desorption. This reaction is independent of the presence of Au nanoparticles and occurs on the TiO₂(110) surface, on which the methoxy groups undergo disproportionation to form CH₃OH and CH₂O.^[25] In stark contrast, we focused on the role played by the Au/TiO₂ interface and demonstrated that a low-temperature channel for selective CH₃OH oxidation to CH₂O opens on Au/TiO₂.

In the case of the Au/TiO₂(110) surface (with 0.4 ML Au deposition) being solely exposed to CH₃OH at 95 K, only the desorption of CH₃OH is observed indicating that no low-temperature methanol oxidation occurs in the absence of coadsorbed oxygen at the Au/TiO₂ interface. The CH₃OH desorption leads to a dominating peak at 297 K, which is assigned to the CH₃OH species bound to Ti⁴⁺ sites on TiO₂(110) (Figure S2).^[25] In addition, a shoulder around 400 K is resolved at the higher temperature side. This peak is related to CH₃OH adsorbed at the Au/TiO₂ interface as supported by the experimental and theoretical results discussed below. By assuming a pre-exponential factor of 10¹³ s⁻¹ and first-order kinetics, the activation energies for CH₃OH desorption from the TiO₂(110) surface and Au/TiO₂(110) interface are estimated to be 0.88 eV and 1.21 eV, respectively, which are in agreement with the calculated values (0.86 eV and 1.13 eV; Figure S15 and Table S2).

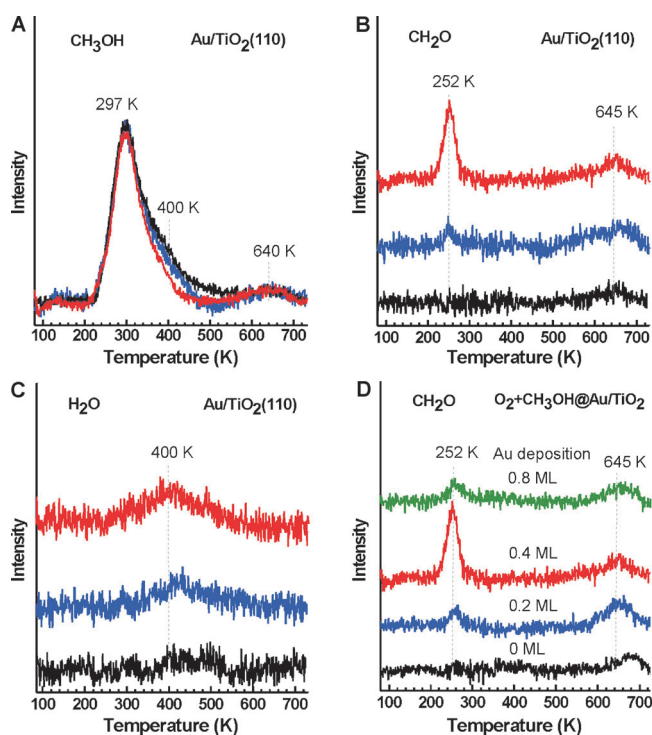


Figure 3. TDS spectra of Au/TiO₂(110) obtained after adsorption of CH₃OH and O₂ at 95 K. The desorption data were recorded for the following species: A) CH₃OH, B) CH₂O, C) H₂O. The spectra in (A), (B), and (C) were obtained after CH₃OH adsorption on Au/TiO₂(110) (black), O₂ adsorption subsequent to CH₃OH adsorption on Au/TiO₂(110) (blue), and CH₃OH adsorption subsequent to O₂ adsorption on Au/TiO₂(110) (red) at 95 K. d) CH₂O desorption from Au/TiO₂(110) as a function of Au coverage obtained after CH₃OH adsorption subsequent to O₂ adsorption on Au/TiO₂(110) at 95 K. The heating rate was 1.5 K s⁻¹.

For the sequential adsorption of first O₂ and then CH₃OH on Au/TiO₂(110) at 95 K, the selective oxidation of CH₃OH to formaldehyde and water takes place at the interface between Au and TiO₂ upon heating to higher temperatures, as clearly confirmed by the appearance of a sharp desorption peak of CH₂O at 252 K and a broad H₂O peak centered around 400 K (Figure 3B,C). The formation of CH₂O and H₂O is accompanied by the consumption of CH₃OH species bound to the Au/TiO₂ interface, while the intensity of the TiO₂-related CH₃OH peak at 297 K remains unchanged (Figure 3A). Importantly, no other products such as H₂, CO, CO₂, and HCOOH are observed in the TDS spectra revealing that the Au/TiO₂ interface exhibits both high catalytic activity and selectivity for formaldehyde production.

Interestingly, when oxygen is adsorbed subsequent to CH₃OH adsorption on Au/TiO₂(110), the formation of CH₂O at 252 K is dramatically reduced (Figure 3), and water desorption from the interface also diminishes accordingly. These findings indicate that the preadsorption of O₂ is crucial for the low-temperature selective oxidation of CH₃OH at the Au/TiO₂ interface, in line with the DFT mechanism (Figure 1C,D; Figure S9). Given that the desorption of CH₂O formed through CH₃OH oxidation is controlled by the reaction, the peak at 252 K yields an activation energy of

0.68 eV for CH₂O formation, in excellent agreement with the calculated result (0.69 eV, Figure 1E,F; Figure S12). In addition, the broad H₂O desorption peak at a higher temperature range is indicative of the recombination of hydroxy species formed by CH₃OH oxidation in accord with the theoretical reaction scenario (Figure 1H,I; Figure S14). Furthermore, the desorption temperature centered at 400 K supports the relatively high diffusion barrier of hydrogen transfer from the Au cluster to an O atom at the perimeter site thus forming OH species (1.1 eV; Figure 1G; Figure S13).

The impact of Au coverage on methanol oxidation at the Au/TiO₂ interface was also investigated. As shown in Figure 3D, no CH₂O desorption is observed at 252 K on the pure TiO₂(110) surface. The CH₂O production increases with increasing Au coverage and reaches a maximum at 0.4 ML. Further increasing the Au coverage to 0.8 ML leads to a significant decrease of the CH₂O yield. The TDS data reveal that 0.4 ML is the optimum coverage of Au to achieve the maximum concentration of interfacial sites. This coverage of Au clusters corresponds to an average particle size of 3–3.5 nm (Table S1).^[19] It has been reported that supported Au nanoparticles of this size are the most active ones for CO oxidation.^[2,10] In addition, it has been proposed that this reaction occurs at dual perimeter sites between Au and TiO₂.^[10] The population of interfacial sites is lowered at higher Au coverage owing to the formation of larger Au clusters (Table S1). These findings provide further evidence for the crucial role of the Au/TiO₂ interface in low-temperature methanol oxidation.

Overall, our experimental and theoretical results demonstrate consistently that the interfacial sites between Au and TiO₂ open a low-temperature reaction channel for the selective oxidation of methanol to formaldehyde and water. Detailed insights into the fundamental mechanism involved in this complex reaction have been obtained, which will impact the design of efficient Au-based catalysts with high reactivity and selectivity in particular for low-temperature alcohol oxidation.

Experimental Section

The first-principles density functional theory (DFT) calculations have been performed using the Car–Parrinello Molecular Dynamics (CPMD) and the Quantum Espresso codes. All the calculations have been performed using spin-polarized GGA + U, Perdew–Burke–Ernzerhof exchange–correlation functional (PBE). The spin-polarized Kohn–Sham equations were solved in the plane-wave and pseudopotential framework using Vanderbilt’s ultrasoft pseudopotential with a cutoff of 25 Ry using the Γ point. In line with our previous work, we made use of the LDA + U implementation and a value of $U = 4.2$ eV.

The HREELS and TDS experiments were performed in a ultra-high vacuum (UHV) apparatus consisting of two chambers connected by a valve. The base pressure was 5×10^{-11} mbar. The upper chamber was equipped with LEED optics and a quadrupole mass spectrometer used to perform TDS experiments. The lower chamber housed a HREEL spectrometer (Delta 0.5, SPECS, Germany) with a straight-through energy resolution of 1 meV. The TiO₂(110) single crystal was cleaned by repeated cycles of sputtering (1 keV Ar⁺, 30 min) and annealing (850 K, 5 min). Typically, about two cycles were followed by one cycle with annealing in an ambient oxygen

environment. The reduced surface was obtained by annealing to 900 K in vacuum. The gold nanoparticles were deposited onto TiO₂(110) using an electron beam evaporator (EBE-4, Specs). A quartz crystal microbalance (QCM) was used to measure the coverage of gold deposited onto the substrate. The background pressure was less than 1×10^{-9} mbar during Au deposition. After deposition, the samples were annealed at 750 K in vacuum for 2 min to ripen and stabilize the Au nanoparticles.^[19]

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