

Electron Transfer From a Semiconductor to a Metal and Its Implication on Photocatalysis for Hydrogen Production

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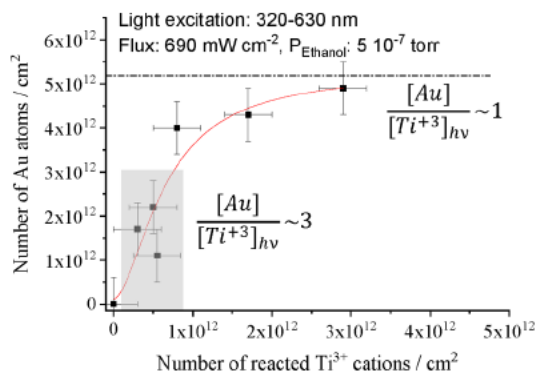
ABSTRACT: Charge transfer from or to a metal deposited on an oxide semiconductor is central to photocatalysis. To probe into this phenomenon, the effect of gold coverage on the chemical state of Ti cations, upon photoexcitation of rutile TiO₂(110) single crystal, was investigated. Photocatalytic reaction of gas phase ethanol (a hole scavenger) on TiO₂(110) and Au_x/TiO₂(110) resulted in the formation of Ti³⁺ cations. Increasing the Au coverage led to a gradual decrease of these Ti³⁺ cations. Under the investigated reaction condition, the “quasi” total consumption of these reduced states was found at a ratio of Au atoms to reacted Ti³⁺ cations close to one: $\frac{[Au]}{[Ti^{3+}]_{hv}} \rightarrow 1$;

this corresponded to about 0.50 at. % of Au/TiO₂. The relationship, which is similar to that of hydrogen production rates, obtained on model and practical photocatalytic systems, suggests that the slow reaction rates, generally observed in photocatalysis, are intrinsic to the metal–semiconductor properties.

INTRODUCTION

Electron transfer reactions between two solid components, one of them at least is in an excited state, such as in a photocatalyst composed of metal clusters on top of a semiconductor, are central to many physicochemical phenomena. Such a system has been studied at the experimental and computational levels^{1–5} for decades. Probably the most known one is the Au/TiO₂.^{6–9} However, limited work on well-defined surfaces is devoted to studying such a system, as a catalyst, upon photon excitation.^{10–12} This study is, in particular, useful for further progress in charge transfer reactions related to energy conversion, which is central to the water-splitting reaction using sunlight. It has now become clear that practical photocatalytic production of hydrogen from pure water using sunlight may not be made possible in the near future.¹³ This is largely because of our limited understanding of the many steps related to electron abstractions from the oxygen anions from adsorbed water/hydroxyls and, to a less extent, of the electron donation to the hydrogen ions of surface hydroxyls. While electron abstraction from oxygen anions of water by a model semiconductor photocatalyst is so far not within reach¹⁴ of that of hydrogen ion reduction that has been experimentally observed numerous times^{15,16} and in some cases modeled.^{17,18} For hydrogen-ion reduction, one needs to use a hole scavenger such as primary alcohols whose thermal reactions on the surface of TiO₂ single crystals were also studied for decades.^{19–22}

In a recent work on the Au/TiO₂(110) rutile model photocatalyst, clusters of Au (with size between 0.4 and 0.8



nm) were prepared, their sizes and dispersion monitored by STM, and then their reaction for hydrogen production from ethanol by mass spectrometry as a function of light excitation intensity was followed.²³ A nonlinear increase of H₂ production with increasing gold coverage was seen. From these experimental results it appeared that the key factor determining the rate of reaction was the Au intercluster distance. Therefore, it was inferred that excited electrons diffusion length within “TiO₂ surface and near bulk” to “gold clusters” is the most plausible explanation. Moreover, in the same work it was shown by pump–probe transient absorption spectroscopy measurements of Au/TiO₂ powder that excited electrons are transferred from the conduction band of TiO₂ to Au particles within the first picoseconds after UV excitation.

The fate of excited electrons in the conduction band (CB) of a semiconductor and its “possible” transfer to a metal cluster has received considerable interest in powder systems. An extensive body of work was conducted by EPR on TiO₂ and Au/TiO₂ under UV excitation in order to study these charged species. Signals related to Ti³⁺ cations were observed in EPR studies of powder Au/TiO₂ and attributed to different types of

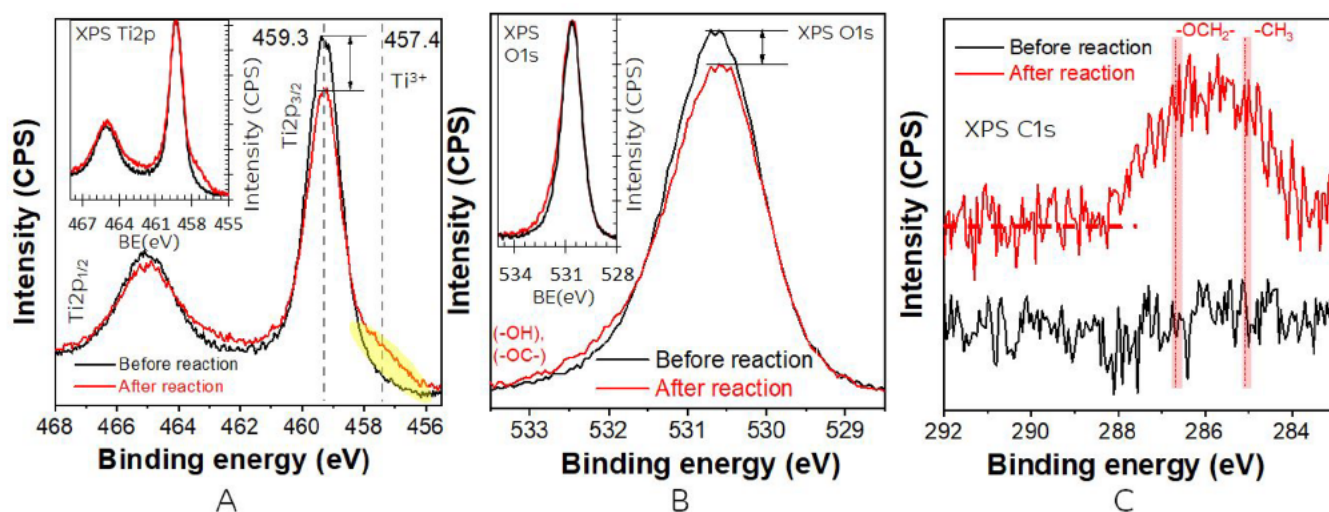


Figure 1. (A) Ti 2p, (B) O 2p, and (C) C 1s core level spectra of the freshly prepared oxidized rutile $\text{TiO}_2(110)$ surface (black) and after light excitation in the presence of ethanol at 5×10^{-7} Torr (red). The insets in A and B are the corresponding intensity normalized spectra of the main ones. The thick horizontal dash line in C indicates the absence of oxidized products while the vertical columns point to the binding energy positions of the methyl group of ethanol at about 285.0 eV and to the carbon of the ethoxy group at about 286.5 eV. The decrease of the intensity of the O 1s after reaction is attributed to screening effect by the ethoxy species while part of that of the Ti 2p of Ti^{4+} after reaction is due to its reduction to Ti^{3+} .

surface and bulk species. When the Au/ TiO_2 system is excited with visible light (in particular in the presence of a hole scavenger), evidence of a weak signal of Ti^{3+} also appears. Since visible light does not excite TiO_2 the appearance of Ti^{3+} is viewed as an injection of an excited electron from Au surface plasmon into the conduction band of TiO_2 . In other words, there are evidence of charge transfer both ways, which evidently will affect the rate of electron transfer to hydrogen ions. So far, EPR of TiO_2 single crystals has not been successful and therefore no work on model system using EPR is possible. A few studies have also used IR spectroscopy to monitor changes in the background attributed to buildup of electrons just below the CB including one study on model systems,²⁴ yet no work on Au/ TiO_2 powder or single crystals under photoexcitation is known in that regard. In general, the Ti^{3+} signal by EPR or the background rise of the IR signal, in the 1000 to 4000 cm^{-1} range, upon excitation are studied at below ambient temperature and in vacuum, because both are suppressed by the presence of gas phase molecular oxygen, water, and lattice relaxation.

Focusing on the electron transfer part of H^+ (of surface hydroxyls), H_2 production is commonly described by a few steps in which electrons are excited from the valence band (VB) to the conduction band (CB) of the oxide semiconductor material (upon excitation). This may be followed by excited electron transfer to a metal particle on top of the oxide surface. This step is generally rationalized by the fact that, for supported metal photocatalysts, metals have work function values greater than those of their oxide counterparts. Part of these electrons may then be consumed in the process of H^+ reduction to atoms, leading to the formation of H_2 molecules upon their recombination. This is not necessarily the only transfer that occurs, and many other factors affect the reaction rate.^{25–28} There is, however, a lack of consensus on the role of the metal in trapping excited electrons from the CB. The argument for this is the natural presence of a Schottky barrier. The argument against this invokes the observation that Au clusters on TiO_2 are already negatively charged and by

corollary, their role might be limited to the catalytic recombination of hydrogen atoms²⁹ to molecular hydrogen since the oxide semiconductor cannot.

To probe into the possibility of charge transfer at the Au/ TiO_2 interface during and after reaction in the presence of photons, the effect of gold coverage on $\text{TiO}_2(110)$ single crystal via the photoreaction of ethanol (a hole scavenger) on the formation of Ti^{3+} cations is studied. Each surface was prepared with a fresh Au deposition, with varying concentrations. The surface was then subject to photocatalytic tests in the XPS spectrometer chamber at a pressure of 5×10^{-7} Torr of ethanol for 2 h. Post-reaction analysis showed the formation of Ti^{3+} cations with a concentration inversely dependent on the content of Au atoms on the surface.

EXPERIMENTAL SECTION

The rutile (110) single crystal ($10 \times 10 \times 1 \text{ mm}^3$) was purchased from MTI and mounted onto a Ta sample plate by spot-welding using Ta stripes. XPS experiments were performed in a UHV system equipped with a built on purpose resistive heating Au doser, comprised of a "V"-shaped tantalum filament and an ultrahigh purity grade Au wire wrapped around it (from Goodfellow). The filament was spot-welded to two copper pins of a high current electrical feedthrough. Prior to the dozer utilization, Au wire was melted into a droplet during the degassing and conditioning procedure, assuring stable and reproducible flux during the deposition. The surface was prepared by cycles of Ar^+ -sputtering (30 min, 1 kV, ca. 10 mA emission current, $5 \mu\text{A}$ (sample current), and pressure of about 1×10^{-5} mbar and annealing to about 750–800 K until a contaminant-free surface composition was obtained; checked by the absence of XPS C 1s signal. Once clean, the sample was further oxidized by annealing in about 1×10^{-6} Torr of oxygen for 60 min. During annealing the sample, temperature was monitored with an IR Sirius pyrometer (Process Sensors). Different sub monolayer coverages of Au were vapor deposited onto a freshly prepared preoxidized $\text{TiO}_2(110)$ at room temperature. UV–visible light irradiation was conducted

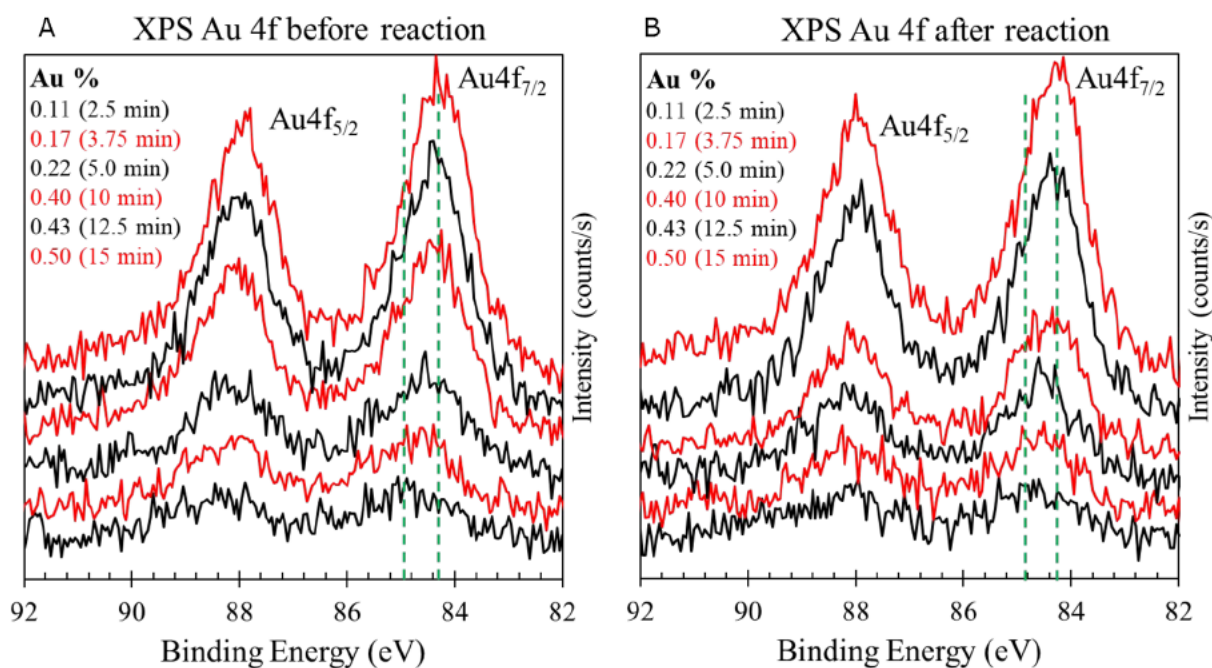


Figure 2. XPS Au 4f core levels of Au/TiO₂(110) rutile, as a function of coverages before (A) and after (B) the photoreaction with ethanol at room temperature; ethanol/water (m/z 18/ m/z 31 = 0.35) at a total pressure inside the chamber = 5×10^{-7} Torr under UV-vis excitation (320–630 nm) and a flux of 690 mW cm^{-2} . Each spectrum was prepared from a fresh surface. The lines are guide to the eyes.

through a sapphire window using a Xenon Arc 300-W MAX-303 Asahi Spectra Xe lamp. The lamp delivered 690 mW cm^{-2} over a range of wavelengths from 320–630 nm (at a distance of ca. 15 cm). The temperature change during illumination was minimal because the excitation source did not contain IR light. Each Au covered surface corresponds to a complete set of experiments starting from a clean oxidized surface.

Ethanol photo-oxidation was done by backfilling the analysis chamber with its vapor at 5×10^{-7} Torr followed by exposure to light using the xenon lamp for 120 min. The inlet into the chamber of ethanol vapor was monitored with an RGA mass spectrometry (Figure S1). In addition to the pattern of ethanol (m/z 31, 45, 27, 15, and 46), the presence of m/z 18 is also noticed; the ratio m/z 18/ m/z 31 was about 0.35. After each reaction XPS C 1s, Ti 2p, Au 4f, and O 1s lines were collected. Quantifications (atom%) were conducted using the following sensitivity factors Ti 2p: 1.798, O 1s: 0.711, C 1s: 0.296, Au 4f: 5.24; all with respect to F 1s signal. A representative set of figures is shown in Figure S2.

RESULTS AND DISCUSSION

We may first investigate changes that occurred on the Ti 2p, and O 1s lines, of clean TiO₂(110), that did not contain Au, after the photocatalytic reaction of ethanol was conducted. Figure 1 presents XPS Ti 2p, O 1s, and C 1s lines before and after reaction with ethanol/water (m/z 18/ m/z 31 = 0.35) at a total pressure inside the chamber = 5×10^{-7} Torr under UV-vis excitation (320–630 nm) for 120 min at about 300 K. Before reaction the Ti 2p at $459.2 \text{ eV} \pm 0.15 \text{ eV}$, the O 1s line at $530.5 \text{ eV} \pm 0.15 \text{ eV}$, shape and binding energy positions and the absence of surface contamination (the removal of the XPS C 1s carbon) were all consistent with a clean and oxidized TiO₂(110) surface. After reaction, changes in the three lines have occurred. A decrease of the signal of Ti⁴⁺ cations (at 459.3 eV) is seen together with the appearance of a signal at its lower binding energy side, starting from 456 eV. This signal is

attributed to Ti^{x+} (with $0 < x < 4$) of the TiO₂(110) surface and near surface; see the highlighted area in yellow in Figure 1A. For simplicity, it will be referred to as Ti³⁺. The integrated peak area ratio of the Ti³⁺ to Ti⁴⁺ is found to be close to 0.1. It is not possible to distinguish between the signals originating from the top layer or the few layers underneath, in addition, for these reduced states (photoelectron kinetic energy ca. 1000 eV). Because the catalytic photoreaction involves bulk excitation it is highly likely that this signal originates from deeper layers, away from the surface, in addition. It is also important to mention that in general this signal is attributed to reduced Ti cations upon the removal of surface oxygen ions that leave behind two electrons per ion removed (as an oxygen atom). UV excitation, at room temperature, of TiO₂ does not remove oxygen anions, this signal is therefore not associated with surface oxygen vacancies.

Signals related to Ti³⁺ cations are observed during EPR studies on TiO₂ powder after photon excitation in vacuum and generally at low temperature, even in the absence of a hole scavenger,^{30–34} although with a much less intensity for the latter case. Other work has also shown a signal by IR spectroscopy, attributed to conduction band electrons and shallow traps (with energies less than 0.5 eV), both in static and dynamic conditions. In this work, we have not observed Ti³⁺ cations in the absence of ethanol (hole scavenger). The XPS O 1s signal showed some changes mostly at the high binding energy side which is due to the buildup of surface ethoxides and associated hydroxyls, from the dissociative adsorption of ethanol ($\text{CH}_2\text{CH}_2\text{-O-(a)} + \text{H-O-(a)}$). A slight broadening due to some metallic states formed after reaction cannot be ruled out – Doniach-Sunjc broadening³⁵). The C 1s showed a typical spectrum of ethoxides species as evidenced by the lines due to both groups (the methyl and alkoxy groups at about about 285.0 and 286.5 eV respectively). It is worth noting that surface carboxylates are not formed; these species need the presence oxygen radical species which is typically

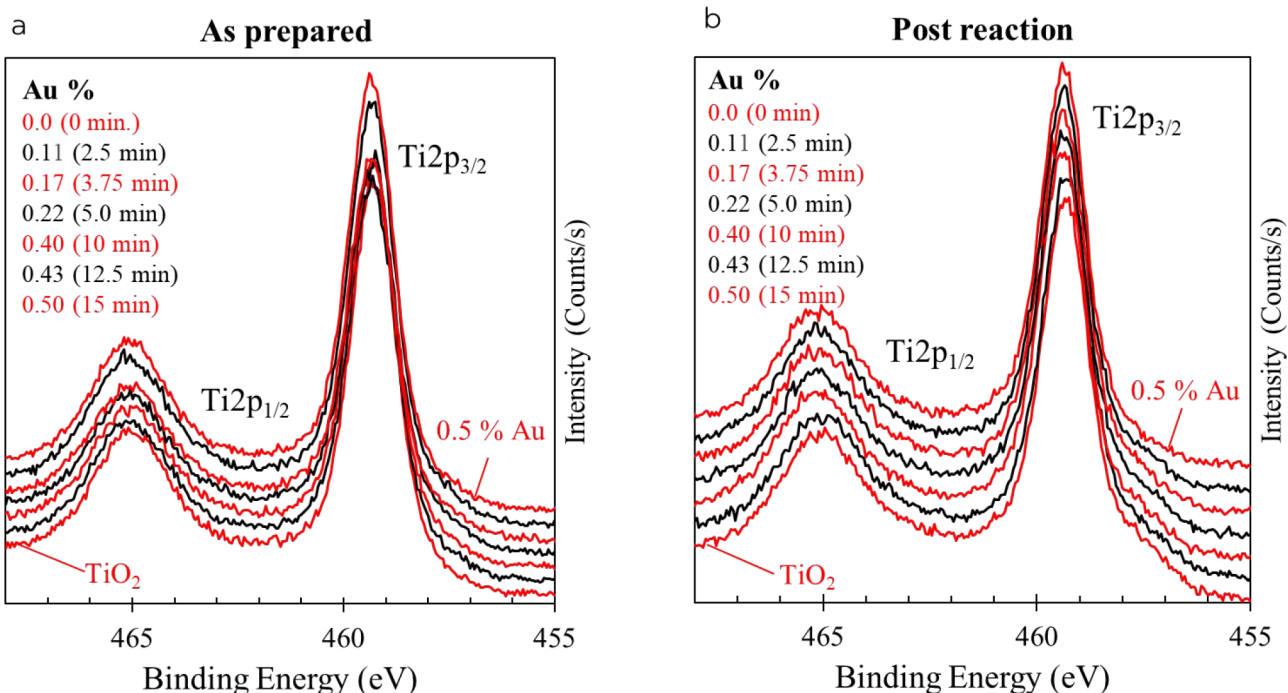


Figure 3. XPS Ti 2p of the fresh as prepared Au/TiO₂ (110) rutile surface and the same after photocatalytic reaction with ethanol/water at room temperature. Ethanol/water (m/z 18/ m/z 31 = 0.35) at a total pressure inside the chamber = 5×10^{-7} Torr under UV-vis excitation (320–630 nm) and a flux of 690 mW cm⁻².

provided by the addition of molecular oxygen in the gas phase during photo-oxidation^{36,37}).

A similar set of experiments was conducted on Au/TiO₂ (110) surfaces. A clean and oxidized surface was prepared for each experiment with the methodology described in the [Experimental Section](#). [Figure 2](#) presents the XPS Au 4f collected spectra of the “as prepared” surfaces and those obtained after the photocatalytic reaction. A nonlinear but gradual shift of the XPS Au 4f core levels from higher to lower binding energy was observed with increasing coverage. The binding energy of XPS Au 4f_{7/2} decreased from 84.8 eV for the initial coverage of 0.11 at. % to 84.3 eV for the final coverage of 0.50 at. %. This has been seen in many other works before.³⁸ The shift is attributed to a particle size effect,³⁹ where, for metal clusters with a subnanometer size, the process of photoemission leaves an unscreened hole. After the photo-reaction of ethanol, the binding energies shift of XPS Au 4f core level peaks was still noticed although with a slight decrease of their fwhm, most likely due to a marginal sintering as observed before by STM in similar reaction conditions.²³

The presence of Au clusters on top of TiO₂(110) has resulted in one main difference in the probed electronic state of Ti 2p after reaction. A gradual disappearance of the reduced states (Ti³⁺ cations) as a function of Au coverage occurred. By about 0.50 at. % of Au, almost all reduced states have disappeared. The main spectra are presented in [Figure 3](#) a and b together with [Table 1](#). A gradual decrease of the, after reaction Ti³⁺ cations, is noticed with increasing Au coverage. It is important to mention that each experiment was conducted separately where the Au atoms were removed from the surface of TiO₂(110) by successive Ar⁺-sputtering and annealing. Once an oxidized clean surface is obtained Au cations were dosed again at a given coverage ([Figure 2](#)). The corresponding XPS C 1s spectra are presented in [Figure S3](#). All spectra contain the signature of ethoxide species at about 285 and

Table 1. At. % and Number of Au Atoms on a TiO₂(110) Rutile Single Crystal, Together with the Fraction of Ti³⁺ Cations Formed and Reacted upon the Photocatalytic Reaction of Ethanol^a

Au at. %	No. of gold atoms/cm ²	fraction of Ti ³⁺	fraction of Ti ³⁺ that has reacted	No. of atoms of Ti ³⁺ that has reacted/cm ²
0	0	0.1	0	0
0.11	1.1×10^{12}	0.089	0.011	5.5×10^{11}
0.17	1.7×10^{12}	0.094	0.006	3.0×10^{11}
0.22	2.2×10^{12}	0.09	0.01	5.0×10^{11}
0.40	4.0×10^{12}	0.084	0.016	8.0×10^{11}
0.43	4.3×10^{12}	0.066	0.034	1.7×10^{11}
0.49	4.9×10^{12}	0.042	0.058	2.9×10^{11}

^aThe raw data are presented in [Figures 2, 3, and S2](#).

286.5 eV, as observed in [Figure 1C](#). There is a minor signal developing at 289–289 eV which is that of –COO- group with increasing gold coverage. The presence of an oxidized route may appear contradictory to the role of Au in acquiring the electronic charges from Ti³⁺, yet it is explained considering the complete photoreaction steps on Au/TiO₂. The ejection of a CH₃ radical during the reaction leads to a slight buildup of formates, as has been seen previously.^{40,41,38}

Although [Figure S4](#) shows the presence of d-electrons due to the creation of these reduced states, at about 1 eV below E_F , the very weak signal-to-noise prevented quantitative analysis. The fraction of Ti surface atoms in the Ti³⁺ oxidation state after the photocatalytic reaction as measured using the Ti 2p lines and as a function of Au coverage is shown in [Figure 4a,b](#). [Figure 4a](#) shows the as computed peak areas of Ti³⁺ (the individual spectra with the difference being highlighted are shown in [Figure S2](#)). A monotonic decrease of the % of Ti³⁺ cations with increasing Au at. % is seen. At about 0.5 at. % of Au, the Ti³⁺ peak area is virtually zero. [Figure 4b](#) presents the

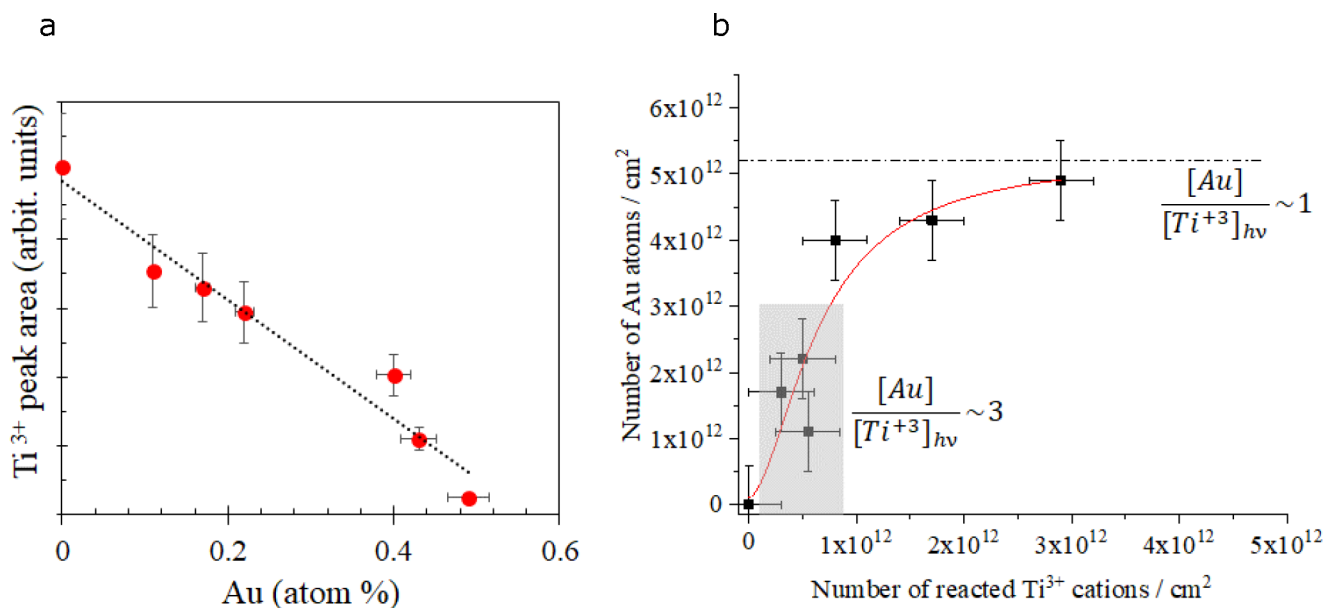


Figure 4. Decrease in the Ti³⁺ peak area as a function of Au atomic% on TiO₂(110) and (b) the number of Au atoms on rutile TiO₂(110) as a function of number of Ti³⁺ cations that has disappeared (with respect to the pristine surface) after the photocatalytic reaction with ethanol/water at room temperature. Ethanol/water (m/z 18/ m/z 31 = 0.35) at a total pressure inside the chamber = 5×10^{-7} Torr under UV-vis excitation (320–630 nm) and a total light flux of 690 mW cm^{-2} .

same data plotted taking into consideration the total number of atoms of Au in the different experiments and the number of Ti³⁺ cations that have reacted. In other words, it is a relationship between the number of Au atoms that have “possibly” trapped electrons during the photoreaction and the number of Ti³⁺ that have disappeared. The shape of the dependence has some logarithmic part (although it is best fitted with an inverse cubic function) where at high enough numbers saturation has occurred. As can be seen, the asymptote is reached at about 1 Au atom per electron consumed and there is little incentive to further increase their amount, this is equivalent to about 0.50 Au at. %. This is in line with almost all studies in photoreaction of alcohols using noble metals on top of TiO₂ powder and probably most other oxide semiconductors; where the optimal catalyst compositions is often composed of less than 2 wt % of the deposited noble metal^{42–50} (1.5 wt % of Au on TiO₂ is about 0.6 at. % Au). From the derivative of the fitting function of the data, the maximum number of Au atoms needed to trap one electron at very low coverage can be obtained and it is found to be about 3. That is probably best explained statistically, at very low coverage electrons have less chance to travel far enough to reach gold atoms and are therefore tapped in their path (wavefunction) and stay there for a period of time.

Returning back to the initial question, do these Ti³⁺ cations disappear because one electron per Ti cation is transferred to Au clusters which in turn reduce H⁺ cations to atomic hydrogen, or do H⁺ cations are reduced to atomic hydrogen on the semiconductor surface and the presence of Au atoms is for their catalytic recombination to molecular hydrogen only? Probably putting the facts first would help addressing the question.

1. Reduced Ti³⁺ cations are formed within TiO₂ upon photocatalytic reactions of a hole trapping, reactant such as ethanol in this work.
2. A metal is needed to make the reaction, in the absence of a metal the rate is 1–2 orders of magnitude slower

and this seems to be independent from the nature of the semiconductor in powder form, TiO₂, SrTiO₃, ZnO, CdS, and g-C₃N₄ to name a few.

3. The presence of Au (as in this work) suppresses the formation of Ti³⁺ cations.
4. A small surface coverage of a metal is needed (typically a few %) increasing the coverage does not increase the reaction rate (in some cases a mild decrease occurs).
5. Hydrogen ions reduction is orders of magnitude slower than the electron transfer from rate from TiO₂ to Au (or from a semiconductor to a noble metal in general).

If the presence of Au clusters is only linked to the hydrogen atom recombination reaction one would not have expected reaching such a fast asymptote as shown in Figure 4b. In a previous work, we have observed on Au/TiO₂ powder, a gradual quenching of the PL that started to saturate at a much higher loading than the one observed here (about 10× higher).⁵¹ Others have also observed an almost total quenching of the PL signal at 0.15 ML Au/TiO₂ powder.⁵² If one may consider the quenching of TiO₂ photoluminescence (PL) as an indication of electron transfer from the semiconductor (TiO₂) to the noble metal (Au) then the results reported in this work are dissimilar to PL results that were conducted in noncatalytic conditions. The fast-reaching saturation (in terms of metal%) both for removing Ti³⁺ cations and for making hydrogen molecules seems to be linked to the “limited potential” of these clusters to acquire excited electrons from the semiconductor and the “limited potential” of TiO₂ to make Ti³⁺ cations. Since the hydrogen ion reduction is orders of magnitude slower than the electron transfer to Au clusters, the rate is thus limited by the former step. In other words, there is no need for more metal atoms to be deposited on the surface. This, and the time-discrepancy between both (the fast (and limited) electron transfer to gold atoms and the slow electron transfer to H⁺) appear to be the two most important reasons for affecting the overall reaction rate.

CONCLUSIONS

The effect of gold coverage on TiO₂(110) single crystal and photoreaction of ethanol was investigated by X-ray photoelectron spectroscopy. In the presence of gas phase ethanol (as a hole scavenger), a gradual disappearance of the Ti³⁺ XPS signal with increasing the coverage of Au atoms occurs. The Ti³⁺ signal is only observed when ethanol was present as a reactant. Fitting the experimental results suggests that an asymptote for Au atoms to electrons ratio approaching unity at high coverage is reached. The relationship suggests that electron transfer occurs from the excited semiconductor to Au atoms during the photocatalytic reaction. Since a similar Au coverage range is seen for the photocatalytic hydrogen production on the same surface it seems reasonable to conclude that the role of Au (a noble metal) is to trap electrons from TiO₂ (a semiconductor).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.2c04025>.

Mass spectrometry of ethanol inside the UHV chamber at 5×10^{-7} Torr pressure; XPS Ti 2p spectra for the Au/TiO₂(110) series and the difference spectra before and after photoreaction; XPS C 1s spectra obtained after the photoreaction with ethanol/water at room temperature; XPS valence band region of TiO₂(110), and 0.11 at. % Au/TiO₂(110) before and after photoreaction (PDF)

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Notes

The authors declare no competing financial interest.

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