

Catalysis and Photocatalysis by Nanoscale Au/TiO₂: Perspectives for Renewable Energy

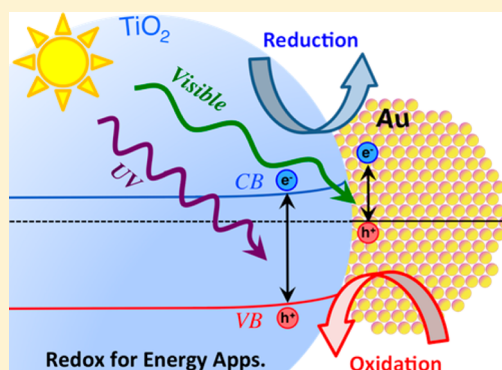
Dimitar A. Panayotov,[†] Anatoly I. Frenkel,^{‡,§} and John R. Morris^{*,§,¶}

[†]Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

[‡]Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York 11794, United States

[§]Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24060, United States

ABSTRACT: Nanoscale gold–titania (Au/TiO₂) catalysts may provide the right combination of electronic structure, structural dynamics, and stability to facilitate wide ranging chemical transformations, including reactions for utilization of renewable energy sources. The Au/TiO₂-based systems have also emerged as promising photocatalysts capable of promoting light-induced production of hydrogen and other renewable hydrocarbon-based fuels. This Perspective summarizes some of the fundamental aspects and concepts built over the last 30 years that help explain the catalytic and photocatalytic performance of Au/TiO₂ materials. The application of emerging operando methods, based on synchrotron experimental techniques, is also briefly highlighted within the context of key catalytic reactions that may have fundamental importance in renewable energy production and storage.



For nearly all of human history, gold has been sought after for its natural beauty, immutability, and unique balance of malleability and durability. In contrast, gold had virtually no value in the chemical sciences until the remarkable discovery, first by Hutchings¹ in 1985 and then by Haruta et al.² in 1987, that, when subdivided to nanoscale dimensions, gold can catalytically oxidize CO to CO₂ at subambient temperatures. The next 30 years saw an exciting period of scientific interest in gold that focused intently on uncovering the potential of nanoscale gold as a catalyst.³ Scientists from different branches of experimental and theoretical research combined their efforts to develop a deep fundamental understanding of the factors that control the unusual catalytic behavior of nanoscale gold and to advance formulations of supported Au-based catalysts.^{3,4} Beyond thermal catalysis, nanoscale gold has also been shown to facilitate photocatalytic processes in the ultraviolet (UV) and visible range, even for large band gap semiconductor supports. Thus, a new research field in catalysis science emerged: the “Catalysis and photocatalysis by nanoscale gold”.⁴

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Developing a detailed scientific understanding for why gold morphs from inert to catalytic as individual particles approach the nanoscale is a formidable challenge because electronic and physical properties of the material cannot be independently controlled for systematic studies. In thermal catalysis, one must identify the effects of energy, geometry, and electronic structure on mechanistic pathways.^{4,5} In photocatalysis, knowledge of the optical response of the catalyst, the dynamics of charge photo-generation and separation, and the photophysical mechanisms of charge transfer must be untangled to provide fundamental insight into the overall chemistry.⁴ Moreover, thermal chemistry and thermal effects almost always accompany photochemistry. Distinguishing the thermally driven stages of a reaction from the photoinduced steps has been, and remains, one of the major challenges in this field.

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While isolated gold clusters are known to be reactive, the active gold particles are typically dispersed on a support, which

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adds an additional layer of complexity and richness to the chemistry. Titania-supported gold particles, Au/TiO₂, have emerged as the most important model and practically applied gold-based catalyst.⁴ Many of the same properties that are responsible for the use of pure TiO₂ as a heterogeneous catalyst,^{6,7} including its high stability, reducibility, and electronic structure, make the material an ideal support for Au-based catalysts. Au/TiO₂ exhibits remarkable performance in the dark for catalytic oxidation of small molecules such as CO and H₂, as well as in selective chemical transformations (hydrogenation, oxidation, etc.) of complex organic molecules.^{3,4,8} In oxidation reactions, the initial adsorption and activation of oxygen is characterized as oxygen atoms interacting with perimeter Au atoms and the coordinately unsaturated (cus) Ti⁴⁺ site on TiO₂ at the gold/titania interface.^{9–11} Scientists also established that these same interfacial sites can promote the activation of C–H and C–O bonds,^{8,9} leading to the selective deoxygenation of organic acids, an important step in the utilization of renewable energy sources such as biomass.^{3,8} Beyond thermal chemistry, Au/TiO₂ systems have emerged as promising photocatalysts⁴ capable of promoting catalytic hydrogen production from renewables. Photocatalytic reduction of CO₂ into renewable hydrocarbon-based fuels over Au/TiO₂-based catalysts¹² has also shown promise in the development of artificial photosynthesis strategies.

In this Perspective, we highlight some of the fundamental aspects and concepts associated with Au/TiO₂ catalysts with the goal of providing a brief introduction to the topic that may motivate further exploration in this exciting field. In particular, we highlight the synergy between “descriptors”¹³ (energetic, geometric, and electronic) that are responsible for the unique catalytic activity of gold nanoparticles.^{5,13} This discussion provides a platform for introducing advanced approaches for structural and compositional manipulation of nanoscale gold that are designed to provide the right combination of properties for achieving high catalytic activity and selectivity. Equally important to materials development is the challenge of characterizing catalyst structure (geometrical and electronic) in real time and under practical operational conditions.^{5,13} These aspects of Au/TiO₂ catalysis research are discussed within the context of key catalytic reactions that may have fundamental importance in renewable energy production and storage.

Reactivity of Gold: Relativistic Effects, Nobleness, and the *d*-Band Model. Catalysis hinges on the propensity for a surface-binding site or group of sites acting in concert to alter the electronic structure of reactants to weaken (activate) specific bonds and produce intermediates that are poised to transform into more stable products. The products must then exit the site of reaction in a way that returns the catalyst to its original state. The first requirement, activation, does not occur on macroscopic gold because of the well-known relativistic effects for this heavy element, which lead to unusually large *sd* hybridization, and low energy. The reactivity of gold and other transition metals has been described by a simple model presented by Hammer and Nørskov¹⁴ that relates the nobleness of metals to two characteristics: (1) the degree of filling of the antibonding adsorbate–metal *d* states and (2) the degree of overlap between the electronic states of interacting atoms or molecules and the gold *d* states (Figure 1).¹³ These two factors determine the strength of the adsorbate–metal bonding and the activation energy for adsorbate dissociation. Under typical conditions, gold exhibits both a filled antibonding adsorbate–metal *d* state and the largest coupling matrix element. The coexistence of

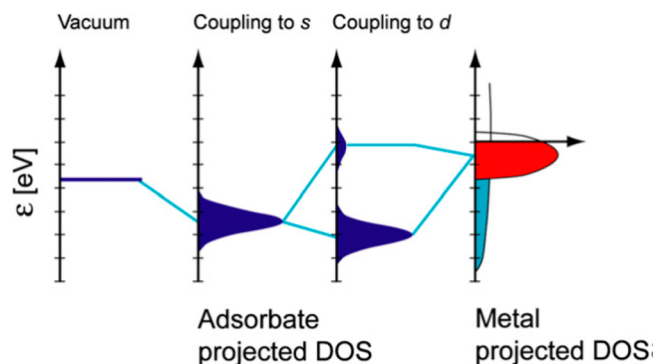


Figure 1. Schematic illustration of the formation of a chemical bond between an adsorbate valence level (dark blue) and the *s* (light blue) and *d* (red) states of a transition-metal surface. The bond is characterized by the degree to which the antibonding state between the adsorbate state and the metal *d* states is occupied. For details, see ref 13 and 109. Copyright 2005 Springer.

the two properties renders bulk gold the most noble metal. For example, clean Au(110)-(1×2) does not dissociatively adsorb or activate hydrogen or oxygen;¹⁵ thus, this surface is completely inactive as a catalyst for hydrogen oxidation. However, the character of the *d* states depends on the width of the band, which changes with coordination number. As the coordination number decreases in late transition metals, the *d* states shift toward the Fermi level.¹³ When the *d* band is higher in energy than the Fermi level, the antibonding orbital for most molecule–surface interactions remains empty, which leads to strong bonding interactions.¹⁶ Thus, adsorbates may become activated at the surface of very small metal particles or particles on substrates that affect the overall electronic structure. For example, when subdivided to nanoparticles of ~3 nm in diameter, gold—when supported on TiO₂—catalyzes the H₂ + O₂ → H₂O reaction even at 200 K with a very small apparent activation energy of 0.22 eV.¹⁷ Beyond particle size, however, the catalytic activity of TiO₂/Au systems depends on a balance between numerous other critical factors.

Nanoscaling Effects on Gold Reactivity. Following the pioneering studies of Haruta et al.² and Goodman and Lai,¹⁸ three different but related types of gold catalyst systems have been the focus of intense research efforts: (1) *isolated model systems*, gold clusters and bulk gold single crystals; (2) *planar systems*, more complex model catalysts composed of size-selected or well-characterized gold nanoparticles deposited onto single-crystal oxide supports; and, (3) *high surface area systems*, more realistic (actual) catalysts composed of gold nanoparticles, often having inexact sizes and structures, deposited on high surface area (powdered or three-dimensional) oxide supports.⁴ Use of these systems enabled scientists to clearly demonstrate how the catalytic activity of Au nanoparticles depends on particle size and shape (Figure 2). One reason for this dependence, beyond how size affects the band structure of the material, is related to the fraction of low-coordinated (LC) corner and edge atoms at the surface of the particles, as effectively illustrated in Figure 2B.

A key result from the work cited above is that structural, dynamic, electronic, and environmental effects influence the catalytic activity and selectivity of supported gold nanoparticles. Various models have been proposed to explain the unique behavior of finely dispersed gold.^{4,5,13} Table 1 highlights the accumulated fundamental knowledge about the nature of these

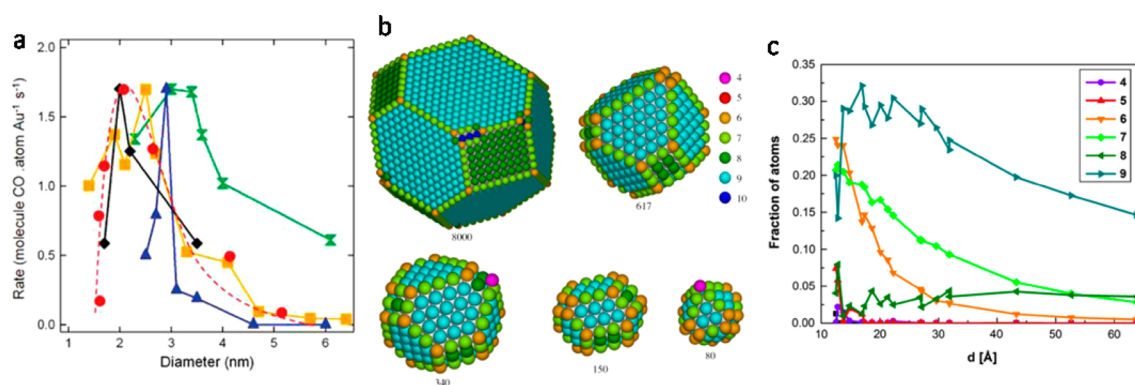


Figure 2. (a) Comparison of the catalytic activity versus Au particle size dependence for oxidation of CO to CO₂ on Au/TiO₂ catalysts prepared by various chemical ways. For details, see ref 19. Copyright 2011 American Chemical Society. (b) Gold particle shapes with lowest energy found in the simulations for different particle sizes. (c) When the particle becomes sufficiently small, the fractions of six- and seven-coordinated corner and edge atoms become comparable to the fraction of surface atoms. Reprinted with permission from ref 20. Copyright 2011 Elsevier B.V.

Table 1. Fundamental Aspects of Nanoscaling

nature of nanoscaling effect	references
A. Predominantly geometric effects	
a. fraction of LC sites, relation to	
size	5, 18–23
shape	19, 20, 23–25
b. bond strain	22, 25, 26
c. unique gold/support interface	
fraction of perimeter Au sites	9, 21, 27, 28
fraction of interfacial Au atoms	23, 29–31
B. Predominantly electronic effects	
a. charge transfer/charge state	32–34
b. quantum size	35–37
C. Adsorbate-induced effects	38
D. Support-induced effects	39, 40
E. Effects of vibrational dynamics	41–43
F. Effects of bimetallic compositions	44, 45

nanoscaling effects, along with key references. It is worth noting that there are many other references that are also important to this field, but an exhaustive list cannot be provided in this short Perspective. (For a more comprehensive review of the field, please see ref 4.)

As can be deduced from Table 1, the complexity of multiple, often synergistic, nanoscaling effects that influence the catalytic behavior of gold necessitates application of combined advanced experimental and theoretical approaches before a complete understanding of the chemistry will be possible.^{3–5,13,23}

Selective Catalytic Processes by Au/TiO₂: Relation to Renewable Energy Production. As researchers continue to uncover fundamental insight into the structure and functionality of Au-based catalysts, others have forged into the use of Au-based catalysts for energy-related applications. Researchers have now effectively demonstrated the potential activity and selectivity of Au-based systems in catalytic conversion of renewable chemicals, including biomass-derived substances, into a diverse array of valued compounds such as fuels, fine chemicals, polymers, and a variety of commodities.^{8,46} Carbohydrates, lignin, vegetable oils, and many other substances extracted from biomass can serve as renewable feedstock and potentially replace petroleum-derived chemicals.^{8,46,47} A variety of catalytic processes based on basic chemical reactions such as oxidation, reduction, hydrogenation, isomerization, etc. have been studied on both model and real

gold catalysts.^{8,46,48–50} Below, we briefly highlight the potential of Au/TiO₂-based systems as catalysts for selective oxidation and selective reduction reactions with compounds derived from renewable sources.

Selective Catalytic Oxidation. The ability of supported nanoscale gold to adsorb and activate oxidant molecules such as molecular O₂, water, and H₂O₂, and thus to promote chemical transformations with high selectivity under mild conditions, make gold systems ideal catalysts for a variety of oxidation reactions. More specifically, these include but are not limited to (a) selective oxidation–dehydrogenation reactions of primary alcohols, aldehydes, and carboxylic acids; (b) selective oxidation of sugars (glucose, arabinose, galactose, and other sugars); and (c) selective oxidation of secondary and poly alcohols.^{8,46} Each of these oxidation reactions has potential for enabling utilization of biomass-derived compounds and other energy-related applications.⁸

For the simple reaction of CO oxidation, both model¹⁸ and real⁵¹ gold catalysts exhibit significant structural sensitivity. The measured turnover frequency for CO₂ production (molecules of CO₂ formed per Au atom per second) showed a volcano relationship with a maximum at Au particle sizes of 2–3 nm (Figure 2A).^{18,19} Analogous relationships have also been found for oxidation of much more complex molecules like D-glucose⁵² and L-arabinose.⁵³ This chemistry is driven by LC atoms on small Au nanoparticles (Au-NPs) that serve as sites for adsorption and activation of reductant molecules, e.g. CO,^{9,10} H₂,^{17,49} arabinose,⁵³ etc. As shown in Figure 2C, the relative number of LC atoms is size and shape dependent.²⁰ Moreover, activation and scission of bonds such as H–H, C–H, and C–O may occur at such sites.^{9,54} Experiments have shown that the adsorption and activation of O₂ on Au/TiO₂ is strongly dependent on the temperature.^{3,28} Thus, the CO oxidation mechanism and the active sites differ for the low-temperature (<320 K) and high-temperature regions (>320 K).²⁸ Some theoretical (density functional theory) studies propose that at low temperature, O₂ activation occurs at Au–Ti⁴⁺ dual perimeter sites via formation of a Au–O–O–Ti intermediate (Figure 3a),⁹ whereas other studies find an adsorption configuration with O₂ directly binding at the Au structure (Figure 3b).⁵⁵ At higher temperatures (~420 K), O₂ can dissociate at the perimeter sites forming O adatoms^{9,56} that can readily interact with bound hydrocarbon intermediates either via nucleophilic attack on C=O and C=C bonds or via activation of weakly acidic C–H or O–H bonds.⁴ The Au–O–O–Ti intermediate⁹ is very similar in character to

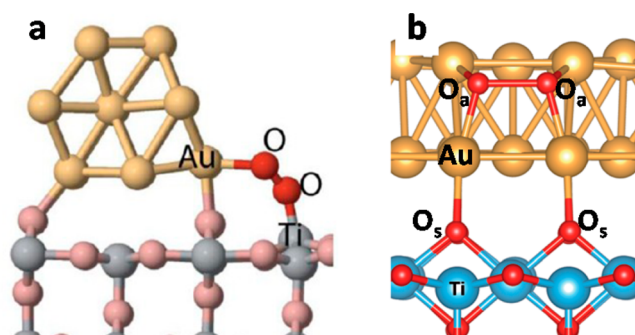


Figure 3. Adsorption configurations of O_2 at the Au/TiO₂ perimeter interface: (a) Formation of a Au–O–O–Ti intermediate via di- σ bonding with Ti–Au dual perimeter sites. For details, see ref 9. Copyright 2014 American Chemical Society. (b) Formation of double linear O_s –Au– O_a structure at the perimeter of Au/TiO₂. Reprinted with permission from ref 55. Copyright 2013 John Wiley and Sons.

the Au-peroxy (Au–OOH) species⁵⁷ that forms in the presence of trace amounts of water in the oxidation of CO. The O/Au and OH/Au species extract charge from the d -band of Au to form weakly basic $\text{O}^{\delta-}/\text{Au}$ and $\text{OH}^{\delta-}/\text{Au}$ species. Acting as nucleophiles, these species can attack C–C and C–O bonds of surface intermediates and activate weakly acidic C–H and O–H groups.⁴ It is well-established that (at low temperatures) small amounts of water can promote oxidation reactions on Au/TiO₂; however, the exact role of O_2 and H_2O remains unclear.^{3,28,58} Both experimental and theoretical investigations find that water-derived species, including hydroxyl groups and hydroperoxide, can be produced directly via reaction of O_2 with H_2O over the catalyst.^{3,28,58} The high oxidation power of hydroperoxide species may play an important role in the selective oxidation of biomass-derived compounds.^{11,46,58,59} Note that the support, TiO₂, can thermally stabilize the active oxygen species, a key factor for improved catalytic performance.^{56,60}

An emerging trend in gold catalysis for biomass transformations is the development of bimetallic systems M–Au/TiO₂ (M = Pt, Pd, Rh, Ru etc.), where the addition of a second metal has been shown to promote the selectivity and improve the resistance to deactivation.^{44,61} Bimetallic M–Au/TiO₂ catalytic systems have been found to be effective in a variety of selective oxidation reactions, including the direct synthesis of H_2O_2 ,⁶² the oxidation of alcohols,⁴⁴ and transformation of biomass to fuel and chemicals.⁴⁵ At present, the nature of synergistic effects in bimetallic catalysts remains poorly understood, and further investigations are needed.^{44,45}

Selective Catalytic Reduction. In addition to oxidative chemistry, supported Au–NPs show potential as unique catalysts in numerous selective reductive reactions with organic compounds.^{8,48,59} An important class of such reactions is the catalytic hydrogenation of unsaturated C–C bonds where hydrogen is supplied either by H_2 dissociation or via a hydrogen-transfer reaction from acids and alcohols.^{8,59} Importantly, nanoscale gold has demonstrated higher activity and selectivity in the hydrogenation of alkenes, dienes, alkynes, and aromatics (with molecular hydrogen) than other noble metals.^{8,48} This was attributed to the beneficial low stability of Au–H species. For most hydrogenation reactions catalyzed by gold, the dissociation of hydrogen at Au–NPs appears to be the rate-determining step.⁴⁸

Another class of reductive reactions catalyzed by supported Au–NPs involves selective hydrogenation of α,β -unsaturated carbonyl compounds (aldehydes and ketones).^{8,48,59} In the presence of gold, the carbonyl group becomes surprisingly

reactive and undergoes preferential reduction (e.g., to form alcohol) under mild conditions, while the C–C double bond remains unreactive. The detailed carbonyl hydrogenation mechanism is still unclear, although a size/shape dependence on activity has been established.⁴⁸ In addition, different oxidation states of gold (Au^0 , Au^{I} , and Au^{III}) are likely important for the activity and selectivity.^{8,48} Furthermore, a different source of hydrogen for the chemoselective reduction of α,β -unsaturated aldehydes can be utilized through the water gas shift (WGS) reaction over Au/TiO₂ at temperatures close to ambient.⁴⁸

The so-called “borrowing hydrogen” concept has also been explored in reductive hydrogenation by gold. It employs a sacrificial hydrogen donor (alcohol, HCOOH, or CO/ H_2O) for the reduction of carbonyl compounds such as aldehydes and ketones (both saturated and unsaturated).^{8,48,59,63} For example, effective N-alkylation of organics, e.g., aniline alkylation by benzyl alcohol to produce a secondary amine, can be catalyzed by Au/TiO₂.^{46,48} Biomass-derived alcohols such as terpenes myrtenol and carveol can be converted via highly selective amination with aniline to the corresponding amines.^{46,64}

Selective Photocatalytic Processes by Au/TiO₂: Relation to Renewable Energy Production. Supported nanoscale gold systems have received special interest in photocatalytic chemistry because of their attractive electronic and optical properties.⁴ The achievement of an optimal combination of key processes, such as (i) solar light harvesting by absorption, (ii) charge separation and electron transport, and (iii) utilization of a generated redox potential in driving the desired chemical reaction, is a great scientific and technological challenge.⁶⁵ The sum and synergy of these processes, in terms of both thermodynamics and kinetics, will determine the efficiency of the desired photocatalytic process.⁶⁶ Of course, the photophysical and photochemical function of supported gold nanoparticles depends on the irradiation regime, i.e., UV or visible, as illustrated in Figure 4.^{61,67,68}

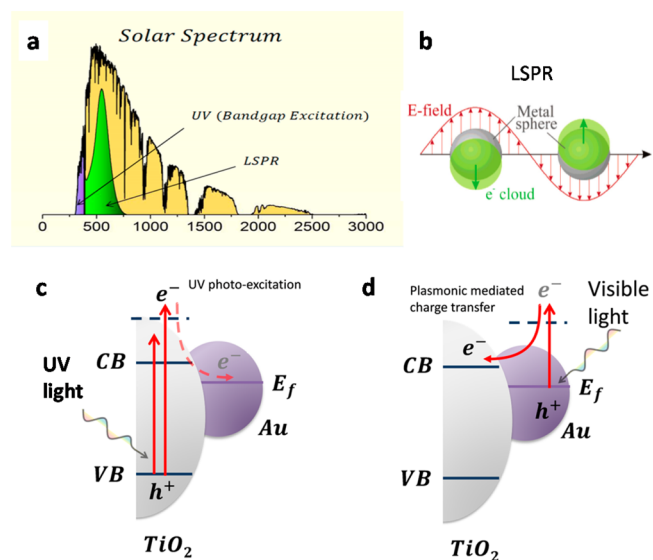


Figure 4. (a) Schematic representation of solar spectrum light-absorption ranges, UV and visible (LSPR), for a Au/TiO₂ photocatalyst. For details, see ref 68. (b) Schematic of plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei. For details, see ref 108. Copyright 2003 American Chemical Society. Schematic of charge photogeneration and transfer for (c) UV and (d) visible light excited Au/TiO₂ photocatalyst. Reprinted with permission from ref 68. Copyright 2016 American Chemical Society.

Upon UV-irradiation of a Au/TiO₂ photocatalyst, Au-NPs can serve as an electron sink for conduction band electrons generated in the light-absorbing TiO₂, thereby enhancing electron–hole pair separation and lifetimes (Figure 4c).^{61,68,69} Such enhanced charge separation is proposed to occur via formation of a Schottky junction, a natural result of the contact between the metal nanoparticle and the semiconductor. However, the importance of this phenomenon for photocatalysis by gold is still under discussion.^{4,61} Charge carriers surviving recombination can reach the surface and be trapped at band gap states where they may become available for redox chemistry via a transfer to adsorbate molecules.

Perhaps most importantly, nanoscale gold systems have been shown to enable photocatalysis in the visible range of the electromagnetic spectrum, even when supported on large band gap semiconductors.⁴ Such visible-light-driven photochemistry is related to the generation of surface plasmons in small Au particles (Figure 4b,d).^{4,68} Local surface plasmon resonance (LSPR) occurs when the photon frequency matches the natural frequency of metal surface electrons (ca. 520 nm for Au) oscillating against the restoring force of their nuclei (Figure 4b).^{61,70,71} The photonic energy can be converted into electronic or thermal energy through the decay of surface plasmons in two pathways: radiative decay transforming plasmons into photons and nonradiative decay producing electron–hole excitations. The optical properties of plasmonic metal nanocomposites, i.e., the bandwidth, position, and intensity of the LSPR, are dependent on parameters such as the nature and morphology (size and shape) of metal nanoparticles and their density in the composite systems. In addition, the nature of the surrounding medium, its dielectric constant and polarization, are also important.^{4,61,72} Several types of plasmon-driven reactions can proceed on excited Au/TiO₂ systems: dissociation of diatomic molecules such as O₂ and H₂, splitting of water, H₂ production from alcohols, liquid- and gas-phase selective oxidation of organics, photocatalytic reduction of CO₂, etc.⁴ For further details on the proposed plasmon-driven photophysical mechanisms, the reader is directed to several recent review articles.^{4,71–73}

Selective Photocatalytic Oxidation. Wide band gap oxides (e.g., TiO₂, CeO₂) are generally considered nonselective photocatalysts because such semiconductors, upon supra band gap (UV) irradiation in aerobic conditions, produce strong oxidizing agents (e.g., hydroxyl radicals, ·OH) that lead to deep oxidation (mineralization) of organic compounds to CO₂ and H₂O.⁷⁴ Deposition of plasmonic Au nanoparticles on TiO₂ can provide photocatalysts with enhanced selectivity and reaction rates several times larger than those observed under dark conditions.⁷⁵ The existence of a correlation between the apparent quantum yield of photoconversion and the LSPR band, the so-called action spectrum, indicates that the visible-light-induced catalytic reaction results from the LSPR effect of AuNPs.⁷⁶ Such correlation has been shown for the performance of Au/TiO₂ in selective photooxidation reactions of methanol,⁶⁷ ethanol to acetic acid,⁷⁶ 2-propanol to acetone,⁷⁶ 1-phenylethanol to acetophenone,⁷⁷ and glycerol to dihydroxyacetone.⁷⁸ Provided such substrates can be derived from abundant and renewable biomass, an efficient selective photooxidation of biomass derivatives can provide a wide variety of value-added chemicals, including food additives, pharmaceuticals, and fine chemicals.^{78,79} In fact, highly selective visible photooxidation (nearly 100% selectivity) of ethanol, glucose, xylose, 2-furaldehyde, 5-hydroxymethyl-2-furfural, and furfuralcohol to the corresponding carboxyl compounds in water has been reported for a Au/TiO₂ plasmonic catalyst.⁷⁹

The same catalyst system is also active under UV irradiation, but addition of Na₂CO₃ (to reduce the oxidation potential of active species) is needed to preserve the high selectivity.^{78,79}

Despite these interesting demonstrations of photochemistry at the Au/TiO₂ interface, a complete mechanistic understanding of such processes, even some of the fundamental aspects of the excitation process, remain issues of some controversy.^{4,77,78} An important area of research that will move the field forward is that which will provide a deeper fundamental understanding of the photophysical mechanisms that govern the transformation of light energy into chemical energy within plasmonic nanostructures.

Selective Photocatalytic Reduction. Conversion of solar photons into energy stored in chemical bonds of compounds (usually termed solar fuels) can help address the global energy challenges and reduce the negative environmental impact of energy production from fossil fuels.^{65,66} It has been confirmed that Au/TiO₂-based composites can be highly efficient photocatalysts for solar fuel production.⁶⁵ For example, hydrogen can be produced by photoassisted splitting of water, where the efficiency of photoconversion and the proposed mechanism depend on the irradiation energy.^{80,81} Upon UV irradiation, Au-NPs play the role of cocatalyst assuring accumulation of electrons photogenerated in the CB of TiO₂ and executing the hydrogen-evolution half-reaction; the photogenerated holes might diffuse to the TiO₂ surface where they complete the oxygen-evolution half-reaction.^{80,82} Upon visible irradiation, the photoexcited LSPR can provide an extra electromagnetic field at the interface between the Au-NPs and the subdomain of TiO₂ that can generate e⁻–h⁺ pairs in the surface region of the semiconductor and promote the water-splitting reaction.^{81,82} Alternatively, the LSPR-excitation of Au-NPs may produce highly energetic electrons in Au-NPs that are injected into the CB of TiO₂, leading to the creation of holes in Au-NPs.⁷¹ In this proposed mechanism, electrons execute the H₂ generation, while holes are quenched by water oxidation to form O₂. Given the limited tendency of water itself to be oxidized to O₂, generation of H₂ by water splitting must be promoted by sacrificial electron donors, such as alcohols.^{82–85} The properties of alcohols (including polarity, polarizability, and oxidation potential) play an important role in catalysis for water/alcohol mixtures containing different species (primary, secondary, tertiary, diol, and triol alcohols).⁸³ In recent work, a linear correlation was established between the rate of H₂ production and alcohol polarity. The free-energy change upon alcohol oxidation is also an important factor.⁸³ Water/methanol⁸⁴ and water/ethanol^{82,85} mixtures are suitable for H₂ production upon either UV or visible irradiation of Au/TiO₂. Liquid-phase UV photoreforming of alcohols produces mainly H₂, where the size of Au-NPs was not a factor for high H₂ production rates.^{82,83} In the gas phase, the selectivity toward H₂ is high, 99%—the remaining products being hydrocarbons (CH₄, C₂H₄, or C₂H₆), CO, and CO₂.⁸⁵ The selectivity toward H₂ increases even higher under solar light simulated irradiation.⁸⁵ Interestingly, H₂ can also be photocatalytically generated from biomass-derived substances, including sugars, starch or cellulose, algae, wood, or grasses.⁸⁵

Another photocatalytic process, often called artificial photosynthesis, is the selective photocatalytic conversion of CO₂ + H₂O mixtures to a variety of products: H₂, CO, HCOOH, CH₄, or CH₃OH. These compounds are highly desirable as solar fuels, especially methanol, because of its high energy density

and chemical utility. The photoreduction of CO₂ includes complex multiple proton–electron transfer steps (with individual activation barriers) and becomes even more challenging when water is used as an electron donor.^{66,86} Over Au/TiO₂, gas-phase CO₂ photoreduction produces mainly H₂ and CH₄ and small amounts of CO, CH₃OH, and C₂H₆.⁸⁷ For the UV irradiation regime, the high capacity of Au-NPs to store electrons serves the highly electron-demanding production of CH₄, where efficiencies 1 order of magnitude greater than that with TiO₂ alone have been achieved.⁸⁷ As one might predict, upon visible irradiation, the Au/TiO₂ system is significantly less active in CO₂ photoreduction.⁸⁷ We note that improvement in efficiency and selectivity toward methane production can be achieved with photocatalysts containing both gold and copper nanoparticles deposited on titania.⁸⁷ It was found that Au–Cu alloy nanoparticles can produce methane with almost complete selectivity (97%) upon irradiation with simulated sunlight. Here, the role of Au is that of light harvester, while Cu is a cocatalyst that binds CO and directs the reduction pathways.⁸⁸ The activation of CO₂ and H₂O occurs via one-electron and one-hole transfer processes, respectively. Then, a series of elementary steps proceeds that involves consecutive transfer of protons and electrons, resulting in the cleavage of C–O bonds and formation of new C–H bonds.⁸⁸ Further theoretical and in situ spectroscopic studies are needed to improve the fundamental understanding of mechanistic elementary steps. This will lead to the synthesis of new photocatalysts with improved efficiency, selectivity, long-term stability, and economic competitiveness.

Future Research Opportunities. The challenge in unraveling mechanistic details of catalysis in general, and Au/TiO₂ systems in particular, is that the link between properties (electronic, structural, thermal) and catalytic performance cannot be revealed when studying simply the prereaction or postreaction states alone. The requirement to characterize the nanocatalysts while they are active, i.e., in real reaction conditions, was the main reason behind the rapid development of *operando* methods, new synchrotron-based experimental techniques and their combined applications in the last 10–15 years.⁸⁹ Because of the importance of atomistic knowledge of electronic, architectural, and compositional details of nanometer-scale catalysts, X-ray absorption spectroscopic (XAS) methods stand out because they are capable of probing changes in NP shape,^{90–94} size,^{92,95} composition,⁹⁶ and charge state.⁹⁶ Importantly, these changes can then be correlated with activity measurements performed in the same XAS experiment by infrared or mass-spectroscopic methods. Long a work-horse technique for NP characterization, XAS is experiencing a renaissance due to the emergence of new synchrotron light sources that support the use of high energy resolution techniques, such as resonant inelastic X-ray scattering (RIXS).⁹⁷ With enhanced energy resolution, detection of changes in *d*-band center, as well as the geometry of adsorbate binding sites on the nanoparticle surface, can be investigated under *operando* conditions.^{98–102} Spatial resolution can be improved by bringing together two probes, the ensemble average XAS and local statistical electron microscopy probes, using a microreactor approach that enables *operando* studies.¹⁰² Another key example of the ongoing research highlights efforts to increase experimental sensitivity to active species (surface or perimeter atoms in monometallic, or a specific compositional motif in bimetallic NPs) by employing a modulation–excitation (ME) approach to XAS data collection.^{103–107}

The ultimate challenge in creating catalysts for specific applications involves first developing an atomic-level understanding of

the motions and energetics that govern the transformation of reactants into products and then applying that insight into designing materials tailored to achieve the desired outcome. Au/TiO₂-based catalysts appear to be excellent candidates and benchmark systems that can be used to advance detailed understanding of interfacial chemical reactions. As new emerging capabilities, such as XAS-enabled technologies and computational advances, continue to develop, they will enable scientists to peer deeper and deeper into the inner workings of heterogeneous reactions and bring us closer to realizing terrific advances in the field of catalysis.

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■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jrmorris@vt.edu. Phone: +1 540 231 2472.

ORCID

Anatoly I. Frenkel: 0000-0002-5451-1207

John R. Morris: 0000-0001-9140-5211

Notes

The authors declare no competing financial interest.

Biographies

Dimitar A. Panayotov is a professor at the Institute of General and Inorganic Chemistry of the Bulgarian Academy of Sciences. His studies are focused on the surface chemistry of gases and vapors adsorbed on thermally, photo-, and electronically excited semiconductor oxides and noble metal/semiconductor oxide catalysts.

Anatoly I. Frenkel is a professor at the department of Materials Science and Chemical Engineering at Stony Brook University. He holds a joint appointment as a senior chemist at Brookhaven National Laboratory. His interests are in mechanistic understanding of advanced nanomaterials by multimodal characterization methods.

John R. Morris received his B.S. from Aquinas College and Ph.D. from Notre Dame, followed by a postdoc at the University of Wisconsin—Madison. As a professor at Virginia Tech, his research focuses on building a fundamental understanding of gas–surface reaction dynamics for energy, environmental, and national defense applications. Group website: <http://www.jrmorris.chem.vt.edu/>.

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