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Aluminum Nanocrystals as a Plasmonic Photocatalyst for Hydrogen Dissociation

by

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ABSTRACT

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Hydrogen dissociation is a critical step in many hydrogenation reactions central to industrial chemical production and pollutant removal. This step typically utilizes the favorable band structure of precious metal catalysts like platinum and palladium to achieve high efficiency under mild conditions. Here we demonstrate that aluminum nanocrystals (Al NCs), when illuminated, can be used as a photocatalyst for hydrogen dissociation at room temperature and atmospheric pressure, despite the high activation barrier toward hydrogen adsorption and dissociation. We show that hot electron transfer from Al NCs to the antibonding orbitals of hydrogen molecules facilitates their dissociation. Hot electrons generated from surface plasmon decay and from direct photoexcitation of the interband transitions of Al both contribute to this process. Our results pave the way for the use of aluminum, an earth-abundant, nonprecious metal, for photocatalysis.
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Chapter 1

**Introduction**

Catalysts are of vital importance in modern chemical industry.\(^1\)\(^-\)\(^3\) To a certain degree, by enhancing the rate and tuning the distribution of products of chemical reactions, catalysts also promote the evolution of human society and change the way people live profoundly. Heterogeneous catalysis is a huge class of catalytic reactions where the reactants and catalyst are in different phase.\(^4\) In most cases, the catalyst is solid phase and the reactants are gas or liquid phase. Reactant molecules can adsorb onto specific sites on the surface of the catalyst and become adsorbates with much lower energy barrier towards chemical reactions. In this way the reaction rate can be enhanced by orders of magnitude than gas phase reaction.\(^5\) Additionally, by carefully engineering the catalyst and reaction conditions, the reaction can be tuned towards a certain product, increasing the selectivity beyond thermodynamic limits.\(^4\)\(^,\)\(^5\)

Conventional catalysts usually require the application of heat and/or pressure to activate the reaction and achieve high efficiency, which puts high demand on the design of reactors and the energy cost of the chemical process.\(^1\) Therefore, it is desirable to develop catalysts that are capable of operating at mild conditions with sustainable energy...
input. Photocatalyst is one promising solution to this problem. A photocatalyst uses the energy of photon, potentially from the sunlight, to drive chemical reactions.\textsuperscript{6-8} For example, it was demonstrated that TiO\textsubscript{2} can be used to split water molecules to hydrogen and oxygen or decompose organic pollutants under light illumination.\textsuperscript{9,10} A new field in photocatalysis is plasmonic photocatalysis.\textsuperscript{11-14} Surface plasmon on metal nanostructures can decay to form hot carriers,\textsuperscript{15-17} and chemical reaction can be induced by hot carrier transfer from the metal to adsorbates. Ethylene epoxidation on Ag nanocubes\textsuperscript{12,18} and hydrogen dissociation on Au nanoparticles\textsuperscript{13,14} have been demonstrated. In this thesis, I demonstrate that Aluminum, an earth-abundant plasmonic metal, can also be used for plasmonic photocatalysis.

Chapter 2 will present the fundamental physics of plasmonic photocatalysis. Surface plasmon resonance, hot carrier dynamics, and surface chemistry induced by hot carrier transfer will be introduced.

Chapter 3 will demonstrate the use of chemically synthesized Al nanocrystals as photocatalyst for hydrogen dissociation. The preparation of photocatalyst and experimental method for probing hydrogen dissociation will be shown first. The dependence of dissociation rate on the wavelength and power of excitation light will be presented and analyzed.

Chapter 4 will present the first-principle calculations that unveil the mechanism of hydrogen dissociation on Al surface under light excitation. The model used for calculation will be introduced. Then the role of hot electron transfer from Al to hydrogen molecule will be analyzed.
2.1. Surface Plasmon and Hot Carrier Dynamics

Surface plasmon is the coupling between electromagnetic wave and collective oscillation of free electrons in metal nanostructures (Figure 2.1a).\textsuperscript{20-22} Surface plasmon can decay, either radiatively through photon emission, or nonradiatively, by transferring its energy to charge carriers in the metal nanostructure (Figure 2.1b).\textsuperscript{15, 17} These carriers are much more energetic than normal, thermally excited carriers and are therefore named hot carriers (Figure 2.1c). In addition to nonradiative decay of surface plasmon, hot carriers can also be generated by direct absorption of photons.\textsuperscript{23, 24} This direct absorption is only efficient when the excitation photons resonate with electronic transitions in the metal involving energy bands with large density of states, e.g. $d$-band in transition metal. The energy distribution of hot carriers depends strongly on the material, shape, and dimension of the metal nanostructure, as well as on the energy of incident photon, as suggested by ab initio theories.\textsuperscript{16, 17}
Hot carriers relax after being generated and different relaxation processes dominate in different time scales. Generally, in 10-100 fs after excitation, hot carriers relax through electron-electron scattering, which transfers the initial electron distribution to a quasi-Fermi-Dirac distribution with effective temperature still much higher than the temperature of the metal lattice (Figure 2.1d). The exact lifetime of hot carriers varies with the material, shape, and dimension of the metal nanostructure and the energy of the hot carriers. Subsequently, around several picoseconds after excitation, the relaxed hot carriers start to interact with the metal lattice through electron-phonon scattering which cools the electrons and heats the lattice. This process can be described by a two-temperature model where the electron temperature and lattice temperature gradually equilibrate. Finally, on the time scale of 100 ps, the metal nanostructure as an entity dissipates heat to the environment through heat transfer.

2.2. Hot Carrier-induced Surface Reaction

Hot carriers can be harvested in a variety of ways for different applications. For example, collecting hot carriers through a metal-semiconductor contact generates photocurrent that enables the design of a photodetector. Another important feature of hot carriers relevant to this thesis is their capability of driving chemical reaction through charge transfer. Since hot carriers are more energetic than normal carriers, they have larger probability of being transferred to molecules adsorbed on the surface of the metal nanostructures. The adsorbed molecules accept hot carriers and form transient ions. The transient ions have different potential energy surface from the neutral molecules due to different electron population level, which induces nuclei motion during the finite
lifetime (several fs) of the ions before the extra carriers return to the metal. In this way the energy is deposited in the vibrational level of the molecules, eventually leading to their dissociation or desorption, as shown in Figure 2.1e.\textsuperscript{12, 18} For example, in photocatalytic epoxidation of ethylene on Ag nanocubes and hydrogen dissociation on Au nanoparticles, oxygen and hydrogen molecules are dissociated by accepting electrons from Ag nanocubes/Au nanoparticles.\textsuperscript{12-14, 18}

![Figure 2.1 Plasmonic Photocatalysis.](image)

(a) Excitation of surface plasmon by a photon. (b) Surface plasmon decays to form electron-hole pair. (c) Hot carrier distribution on the surface of metal nanoparticle. (d) Hot carrier transfer to the antibonding (AB) orbital of adsorbed molecule. (e) Transient electron population change of the molecule changes its potential energy diagram and induces nuclea move. Adapted from Ref\textsuperscript{13}. 

Another theory on hot electron transfer is the direct excitation theory.\textsuperscript{33} When the orbitals of metal and adsorbate hybridize strong enough (which usually requires strong binding between metal and adsorbate), it is possible to directly excite electrons from metal to adsorbate, or more precisely, from a hybridized orbital that extends more into the metal, to another hybridized orbital that localizes more in the adsorbate.\textsuperscript{33, 34}

2.3. Aluminum Photocatalysis

Aluminum, the most abundant metallic element in the Earth’s crust and ten thousand times cheaper than precious metals, has been shown to possess highly promising plasmonic properties.\textsuperscript{35-39} Most notably, Al exhibits low optical losses from the visible to the ultraviolet (UV) spectral regions due to its high electron density and extends the optically tunable range of plasmonic nanostructures beyond that of gold and silver. Applications of Al plasmonics include optical antennas,\textsuperscript{36} plasmon-enhanced photodetectors,\textsuperscript{24, 40} plasmon-enhanced spectroscopy,\textsuperscript{41-43} and display technology.\textsuperscript{44-46} However, direct photocatalysis with Al nanostructures is less explored due to its unfavorable electronic band structure and thus poor affinity for molecules.\textsuperscript{47-49} So far, reported experiments have tried to mitigate this effect by using transition metals to dope Al and reduce the adsorption and reaction barrier,\textsuperscript{50, 51} or using deep UV photons for direct photodecomposition of organic molecules.\textsuperscript{52}
In this chapter, I demonstrate that chemically synthesized aluminum nanocrystals (Al NCs) are capable of photocatalyzing hydrogen dissociation under laser illumination without the use of transition metal dopants, deep UV photons, or extreme reaction conditions such as elevated temperature or pressure. Al NCs supported on $\gamma$-Al$_2$O$_3$ were prepared as the photocatalyst and the isotopic exchange reaction $\text{H}_2 + \text{D}_2 = 2\text{HD}$ was used to monitor hydrogen dissociation. The wavelength dependence of this reaction resolves two different origins of hot electrons contributing to this process, surface plasmon decay and interband transitions.

### 3.1. Photocatalytic Hydrogen Dissociation on Al NCs

Al NCs were synthesized according to the published protocol with minor modifications (see 3.4.1 and 3.4.2 for synthesis method). The Al NCs used in our experiments were nominally 100 nm in diameter, as determined by high-resolution transmission electron microscope (HRTEM) images (Figure 3.1a, Figure 3.4a) with a 3
nm native oxide layer (Figure 3.2b). They were dispersed in $\gamma$-Al$_2$O$_3$ powder at 5 wt % to avoid aggregation. This photocatalyst supports a dipolar plasmon mode at around 460 nm, determined by the UV-vis-NIR extinction spectra of Al NC solutions and by diffuse reflectance spectra of the Al NC/$\gamma$-Al$_2$O$_3$ mixture (see Figures 3.2b and Figure 3.6). The photocatalyst was then loaded into a customized stainless steel chamber with a quartz window (Harrick Scientific Product Inc.) for hydrogen dissociation studies. Research purity hydrogen (H$_2$) and deuterium (D$_2$) were introduced as independent reactants to study the hydrogen dissociation reaction. The detection of HD resulting from catalyst illumination indicates the occurrence of hydrogen dissociation ($\text{H}_2 + \text{D}_2 = 2\text{HD}$). White light from a supercontinuum fiber laser (Fianium, 450–900 nm, see Figure 3.7e for laser spectrum) were used as excitation source. For wavelength dependence measurements, monochromatic light from a tunable Ti:sapphire laser (Coherent, Chameleon Ultra II) equipped with a second harmonic generator was used. The HD concentration in the outlet of the chamber was monitored using a quadrupole mass spectrometer (Hiden Analytical Inc.) in real time.

We observed H$_2$ and D$_2$ dissociation by measuring the HD generation rate in the presence or absence of a white light excitation (Figure 3.1c). The HD generation rate was monitored in real time while keeping the reaction chamber at room temperature and atmospheric pressure. Before laser excitation, a low-level, steady-state HD background level was observed due to HD present in the H$_2$ and D$_2$ gases as an impurity and also due to a very weak spontaneous HD exchange reaction occurring on the photocatalyst. Upon laser excitation (Fianium, 400 mW with laser spot size $\sim$0.1 mm), the HD rate increased rapidly and reached a plateau within 5 min. After the laser was turned off, the HD rate
dropped down to the original background level. This process was repeated multiple times with good reproducibility. To confirm that HD generation was due to the presence of Al NCs in the photocatalyst and not the $\gamma$-Al$_2$O$_3$, which can also activate hydrogen dissociation under certain conditions, the HD generation rates of Al NC/$\gamma$-Al$_2$O$_3$ and pure $\gamma$-Al$_2$O$_3$ were compared. As shown in Figure 3.1d, under laser illumination, Al NC/$\gamma$-Al$_2$O$_3$ showed a high activity for light-induced HD generation while $\gamma$-Al$_2$O$_3$ showed no such reactivity. This indicated that the Al NCs present in the photocatalyst are the active component for hydrogen dissociation.
Figure 3.1 Hot electron-induced hydrogen dissociation on 5 wt.% Al nanocrystal photocatalyst Al NC/γ-Al₂O₃. (a) Transmission electron microscope (TEM) image of Al NCs. (b) High-resolution TEM (HRTEM) of portion of an individual Al NC. The crystalline surface of the Al NC and the native amorphous aluminum oxide layer are resolved. (c) Real-time monitoring of HD generation rate with and without laser excitation (Fianium, 450-900 nm, 4 kW/cm²). Dashed blue lines represent on and off times for
During the photoreaction, the temperature of the photocatalyst increased slightly (<5 K) due to laser-induced heating of the illuminated photocatalyst. To determine whether thermal effects also contributed to the observed reaction, we compared the HD generation rate of the light-induced reaction with the purely thermal catalytic response. The photocatalyst was first illuminated (Fianium, 300 mW) at room temperature, and then heated to 50 °C without laser illumination. The observed HD generation by heating alone was less than 3% of that observed using laser illumination of the catalyst (Figure 3.2a). We also calculated the local temperature increase from laser-induced heating as a function of laser power density and wavelength. The temperature increase was calculated as the ratio of the energy absorbed by the Al NC (product of the laser power density and the absorption cross section of the Al NC) to its heat capacity (see Appendix for detailed calculation). The predicted local temperature increase is below 5 K for all of our experimental conditions (Figure 3.2b). This comparison confirms that the observed hydrogen dissociation reaction on the photocatalyst is light-triggered rather than thermally driven.
3.2. Wavelength and Power Dependence

To better understand the light-induced photocatalytic response, we probed the photocatalyst using excitations at different wavelengths. The amount of HD produced by 30 min of light illumination [Chameleon (680–980 nm) and its second harmonic light
(350–525 nm), laser power kept at 65 mW for all wavelengths] as a function of excitation wavelength is shown in Figure 3.3a as red circles (see 3.4.4 for a detailed description of the wavelength dependence measurement method). A small HD production peak around 460 nm correlates with the dipolar LSPR mode of the Al NCs where hot electrons are produced by decay of the surface plasmon. However, maximum hydrogen dissociation is observed at illumination wavelengths around 800 nm, which corresponds to the interband transitions in Al. At these photon energies, hot electrons are generated by laser excitation of direct transitions between filled and unfilled sp-derived bands of Al, which has a band edge \( \sim 1 \) eV above the Fermi level.\(^{56}\) As a measure of energy transfer from the incident light field to the Al NCs, the absorption cross section of a 100 nm Al NC calculated using Mie theory (see Supporting Information for details) is shown for comparison in Figure 3.3a. The absorption peaks around 460 and 800 nm can be assigned to the localized surface plasmon resonance and the Al interband transition, respectively. Comparison between these two sets of data indicates that excitation of the interband transition of Al results in more HD production even though its absorption cross section is smaller than the LSPR region at shorter wavelengths. Recent work on understanding plasmon-induced hot carrier photophysics indicates that the energy alignment of a metal nanostructure with an adsorbed molecule\(^{57}\) or a semiconductor interface\(^{24}\) ultimately determines which processes, direct photoexcitation or plasmon-induced excitations, will generate useful hot carriers. In Al, the interband transition yields hot electrons with energies approximately 1–1.5 eV above the Fermi level,\(^{17, 24, 56}\) which are energetic enough to transfer to the hydrogen molecule and facilitate dissociation, as supported by first-principles quantum mechanics calculations (discussed in Chapter 4). This is an important and unique feature
of Al-based photocatalytic systems: carrier generation for interband transitions is expected to be very efficient in Al due to its high density of states.

The dependence of the HD generation rate on laser power was measured at 800 nm (interband transition) and 461 nm (LSPR) using Chameleon laser. We observed a linear dependence on the excitation power at both wavelengths, for power densities up to 4 kW/cm$^2$ (Figure 3.3b). The external quantum yield of HD generation is estimated to be $\sim 1\%$. In contrast, for the photocatalytic ethylene epoxidation reaction on Ag nanocrystals a supralinear power dependence of the reaction rate was observed above a laser power density of 300 mW/cm$^2$ and was attributed to a multielectron process.$^{58}$ Here, the observed power dependence remains linear at much higher power densities, suggesting that the hydrogen dissociation reaction studied here is triggered by a single hot electron for both LSPR and interband transition excitations.
Figure 3.3 Wavelength dependence of HD generation on an Al NC/γ-Al₂O₃ photocatalyst. (a) HD production (red circles) on photocatalyst illuminated by monochromatic light [Chameleon (680-980 nm) and its second harmonic light (350-525 nm), 65 mW] for 30 min as a function of excitation wavelength. The error bars represent the standard deviation of multiple measurements. The calculated absorption cross section of a single Al NC surrounded by a porous 100 nm thick γ-Al₂O₃ shell is shown as black curve. (b) Dependence of HD generation rate on laser power using 800 nm (magenta squares) and 461 nm (blue circles) light as excitation sources. Magenta and blue lines are linear fits of experimental data.¹⁹

3.3. Role of the Native Alumina Layer

Another unique feature of the Al NC photocatalyst is the native alumina shell that covers the Al NCs. In our experiment, the native alumina shell is amorphous, as
observed in Figure 3.1b and confirmed by X-ray powder diffraction measurements of the pure Al NC powder (Figure 3.6). Unlike close-packed alumina layers fabricated by physical vapor deposition or chemical vapor deposition that are commonly used as hydrogen barriers,\textsuperscript{59, 60} this native alumina shell is relatively porous, likely allowing hydrogen molecules to reach the Al metal by diffusion to accept hot electrons.\textsuperscript{61-63} Moreover, while Al metal has a high activation barrier for hydrogen adsorption and dissociation, hydrogen molecules can readily adsorb on alumina under room temperature.\textsuperscript{54, 64, 65} Thus, an important role of the native alumina shell of the Al NCs in the photocatalyst is to provide adsorption sites for H\textsubscript{2} and D\textsubscript{2} so that the residence time of H\textsubscript{2} and D\textsubscript{2} on the Al surface is increased, enhancing the probability of hot electron acceptance and hydrogen dissociation. In addition, adsorption of hydrogen molecules on Al and O sites near the Al−Al\textsubscript{2}O\textsubscript{3} interface could stretch the H−H bond, slightly lowering the antibonding orbital and facilitating hot electron injection into hydrogen molecules.\textsuperscript{66-69} The scenario where hot electrons transfer to hydrogen molecules by tunneling through the alumina layer is less likely because of the low electron tunneling probability through the nanoscale alumina layer compared with our measured quantum efficiency.

### 3.4. Method

#### 3.4.1. Synthesis of 100 nm Al NCs:

The Al NCs were synthesized following the published protocol with minor modification.\textsuperscript{53} All solvents and reagents were purchased from Sigma-Aldrich. The
tetrahydrofuran (THF) and 1,4-dioxane were dried and distilled under inert atmosphere before use. Briefly, into a 100 mL flask connected to Schlenk line, 12.5 mL dehydrated THF, 12.5 mL dehydrated dioxane and 6.5 mL of 0.5 M dimethylethylamine alane solution in toluene were injected through syringes. The whole solution was heated to 40 °C in an oil bath under stirring. Then the nucleation and growth of Al nanocrystals were triggered by adding a 0.5 mL solution of 3.3 mM titanium (IV) isopropoxide in toluene. The solution became brown color immediately and then changed to grey green gradually. After 2 hrs, the reaction was quenched by adding 0.5 – 1 mL oleyl acid. The solution was washed with 30 mL toluene twice and then with 30 mL IPA for 3 times. 1000 – 4000 rpm centrifuges were performed to collect the particles between each washing.

3.4.2. Preparation of 5% Al NC/γ-Al2O3 Photocatalyst:

The photocatalyst sample was prepared as a 5 wt% Al NC dispersed on commercial γ-Al2O3 support (Alfa). In a 100mL conical flask containing ~ 95 mg γ-Al2O3 support, a 50 mL IPA dispersion with ~ 5 mg Al NCs was added. The solution was stirred overnight and then centrifuged at 3000 rpm for 10 min to collect the solid sample. The solid sample was vacuum dried at room temperature overnight and ground to a fine powder for photocatalytic measurements. To quantify the mass fraction of Al NCs in IPA solution, a certain volume of IPA solution was centrifuged at 3000 rpm for 10 min to collect the Al nanocrystals. Then the solid sample was vacuum dried at room temperature overnight. The dry solid was collected and weighed to calculate the mass fraction.
3.4.3. Microscopy and Spectroscopy Characterization:

Transmission electron microscopy (TEM) characterization was performed for Al NCs and Al NC/γ-Al₂O₃ sample on a JEOL 2100 Field Emission Gun Microscope with 200 kV acceleration voltage. The particle size distribution was obtained by measuring ~150 nanocrystals. UV-vis-NIR extinction spectra measurement was performed on a Cary 5000 UV-vis-NIR Spectrometer using the IPA solution of Al NCs in the wavelength range from 300 nm to 1000 nm. Powder X-ray Diffraction (PXRD) measurements were performed on a Rigaku D/Max Ultima II diffractometer with Cu Kα radiation (0.15418 nm). The spectra were collected from 35° to 90° at a speed of 0.5°/min. The facets corresponding to the strongest peaks were selected as the Al facet used in our DFT simulations.
Figure 3.4 (a) TEM image of 100 nm Al NCs. (b) Histogram of size distribution of 150 Al NCs. (c) UV-vis-NIR extinction spectrum of Al NCs in iso-propanol. A plasmonic dipolar resonance at ~ 460 nm and interband transition at ~ 800 nm are shown as a peak and a shoulder, respectively.\textsuperscript{19}
Figure 3.5 (a) TEM image of Al NCs on γ-Al₂O₃. Al NCs are labeled in red circles. (b) UV-vis-NIR diffuse reflectance spectrum of 5% Al NCs/γ-Al₂O₃. The plasmonic dipolar resonance blueshifts due to the change of dielectric environment while the interband absorption shown as a dip in reflectance spectrum.¹⁹
3.4.4. Photocatalysis Measurement:

10 mg of 5% Al NC/γ-Al₂O₃ photocatalyst was loaded into a stainless steel reaction chamber equipped with a quartz window (Harrick Scientific Product Inc.). Research purity H₂ and D₂ gas (15 sccm: 15 sccm, Matheson) was flowed through the chamber. For photocatalytic activity and laser power dependence measurements, white light from a supercontinuum laser (Fianium, 450-900 nm, 4 ps, 40 MHz) or monochromatic light from a tunable Ti:sapphire laser (Coherent, Chameleon Ultra II, 150 fs, 80 MHz, 680-1080 nm) equipped with a second harmonic generator (APE Angewandte Physik und Elektronik GmbH) was focused by a 75 mm achromatic lens onto the photocatalyst, with a spot diameter around 0.1 mm. The power of incident light was controlled by a set of variable neutral density filters. The HD concentration in the outlet was monitored in real time with a quadrupole mass spectrometer (Hiden Analytical...
Inc.). The HD enhancement rate was obtained by subtracting the background HD level from that of the “laser on” state.

![Diagram of experimental setup for photocatalysis measurement.](image)

**Figure 3.7** Experimental setup for photocatalysis measurement. (a) Schematic of experiment setup, including: reaction chamber, gas system for introduction of reactants, optical system for laser control and excitation, and mass spectrometer for product detection. (b) Reaction chamber equipped with temperature/pressure control and optical window. The sample is loaded as shown by the white arrow. (c) White light spectrum of the Fianium laser.\(^{13}\)

For wavelength dependence measurements, fundamental (680-980 nm) and second harmonic (350-525 nm) light from the tunable pulsed Ti:sapphire laser was used for excitation. The reaction chamber was first charged with equimolar H\(_2\) and D\(_2\), then the chamber was sealed for 30 min during which the photocatalyst was illuminated by pulses at the selected wavelength. An off-axis parabolic mirror was used to focus the light to a
sub-millimeter spot in order to avoid any chromatic aberration. The average power of the incident beam was fixed at 65 ± 0.5 mW for each wavelength. After the reaction, the gas in the chamber was purged out by argon and the HD produced was recorded by the mass spectrometer.

3.4.5. Electromagnetic and laser heating simulation:

The absorption cross-section of the Al NP was calculated using Mie theory.\textsuperscript{70} The Al NPs were modeled as spherical multi-shells with three different layers: (1) an Al core with a diameter of 100 nm, (2) a 3 nm thick native Al\textsubscript{2}O\textsubscript{3} middle shell, and (3) an outer shell of 100 nm of thickness of porous γ-Al\textsubscript{2}O\textsubscript{3}. The dielectric functions of Al and Al\textsubscript{2}O\textsubscript{3} were taken from Ref.\textsuperscript{71}, while for the porous γ-Al\textsubscript{2}O\textsubscript{3} we used an effective dielectric function obtained using the Maxwell-Garnet model\textsuperscript{72} assuming a matrix of Al\textsubscript{2}O\textsubscript{3} with spherical inclusions of air (50\% volume fraction).

We estimated the maximum temperature increase of the Al NPs when illuminated with the laser following the theory developed in Ref.\textsuperscript{55}. In particular, we assumed that the electron-phonon thermalization occurred much faster than the external heat diffusion and the time separation between laser pulses, which in our case was \(\sim 1/80 \text{ MHz} \sim 12.5 \text{ ns}\). This allowed us to write the maximum temperature increase as

\[
\Delta T_{\text{max}} = \frac{\sigma_{\text{abs}} I}{V_{\text{Al}} \rho_{\text{Al}} c_{\text{Al}} f},
\]

\(\sigma_{\text{abs}}\) being the absorption cross-section of the nanoparticle, \(V_{\text{Al}}\) the volume of the Al core, \(\rho_{\text{Al}}\) the aluminum mass density, \(c_{\text{Al}}\) the Al heat capacity, \(I\) the laser average intensity, and \(f\) the pulse repetition rate. This expression implies that all the energy is absorbed in the Al core, which is a realistic
assumption given the negligible absorption of Al₂O₃ in the spectral range under consideration.
Chapter 4

First-Principle Calculations

We performed periodic density functional theory (DFT) and embedded correlated wave function (ECW) calculations\textsuperscript{73} to gain further insight into the reaction mechanism. Assuming that hydrogen molecules can diffuse through the native alumina layer to the Al surface, a closed-packed Al(111) facet was chosen to model the surface of the Al NCs. Adsorption of the hydrogen molecule parallel to the surface at a bridge site is assumed (Figure 4.1). Of particular interest are charge-transfer (CT) processes from sp-derived Al states into the antibonding orbital of H\textsubscript{2} that may lead to a weakening of the bond and thereby facilitate dissociation. Prior calculations\textsuperscript{13} on an isolated hydrogen molecule have shown that H\textsubscript{2}\textsuperscript{−} has a metastable state located about 1.7 eV above the ground state of the neutral molecule. The bond dissociation energy for this state is 2 eV lower than for the neutral case (2.6 eV vs 4.6 eV).
The ground-state potential energy surface (PES) from embedded complete active space self-consistent field (CASSCF) calculations is shown in Figure 4.2a. The predicted energy barrier for dissociation of adsorbed hydrogen is approximately 2.5 eV, similar to the bond dissociation energy noted above for an isolated H$_2^-$ ion.\textsuperscript{13} Figure 4.2b displays the CT occurring on the ground state PES, as obtained by a Löwdin charge analysis of the embedded CASSCF ground state. As the molecule approaches the Al surface and the reaction barrier along the indicated minimum energy pathway, charge is transferred from the metal to the molecule (the initial small positive excess charge on the hydrogen molecule at large distances is due to an orthogonalization of the Al sp-band with the bonding orbital of H$_2^4$\textsuperscript{48}). CT is already substantial in the ground state; at the transition state (marked by a star in Figure 4.2a/4.2b), the excess charge on the hydrogen molecule is 0.9 electrons. Such a large charge transfer suggests that the electron affinity level of the hydrogen molecule lies very close to the Fermi level of the Al NC substrate (for a Lorentzian level, a charge transfer of one electron would correspond to the affinity level
being resonant with the Fermi level). Because the affinity level is close to the Al Fermi level, it will overlap the photoinduced hot electron distribution. The reaction barrier for hydrogen dissociation will clearly be further lowered after injection of a hot electron from the Al NC into the antibonding orbital.

Figure 4.2 (a) Embedded CASSCF PES for the dissociation of hydrogen on the Al (111) surface. The star marks the transition state (at an energy of 2.5 eV above the ground-state minimum) and the circles refer to points at which DOSs, electron density difference maps or excited state energies are provided below. (b) Löwdin charge analysis of the embedded CASSCF ground state.
same points are indicated by circles and a star as in (a). (c) DFT-GGA DOS projected onto the orbitals of the hydrogen atoms for two different distances from the surface. The inset shows the broadening of the antibonding state in more detail. The dashed line denotes the Fermi energy. (d) Excited state PESs along the reaction pathway indicated in (a) obtained with embedded CASSCF and averaging over the lowest 20 states. The ground state is indicated by triangles while the excited states are indicated by circles. The reaction coordinate (r.c.) is obtained from the bond length ($l$) and the distance to the surface ($d$) according to $r.c. = \sqrt{(l-l_0)^2 + (d-d_0)^2}$, where $l_0 = 0.75$ Å and $d_0 = 5.0$ Å are the parameters at the first point. (e) Interaction-induced DFT-GGA electron density differences as the hydrogen molecule approaches the surface given in units of electrons per Å$^3$; $d$ refers to the surface-molecule distance while $l$ pertains to the H$_2$ bond length.$^{19}$

The electronic density of states (DOS) projected onto the orbitals of the hydrogen atoms obtained from periodic DFT-GGA calculations (compare Figure 4.2c) further corroborates the prediction of significant CT, although DFT will overestimate its extent. As the hydrogen molecule approaches the surface, its bonding and antibonding orbitals are shifted downward in energy, and hybridization with the sp-band of Al leads to broadening of these peaks. The tail of the broad antibonding state now extends below the Fermi level and the state becomes partially occupied at small distances from the surface. This is consistent with the significantly increased charge on the hydrogen molecule (Figure 4.2b). DFT-GGA electron density differences (Figure 4.2e) reveal that the excess negative charge is indeed concentrated outside of the bonding regions of the hydrogen molecule, in accord with a partial occupancy of the antibonding states, while the bonding electron density is decreased. The points on the PES at which the DOS or electron density differences were evaluated are indicated by circles in Figure 4.2a/4.2b).
We also performed excited-state embedded CASSCF calculations along an approximate minimum energy pathway (indicated in Figure 4.2a) to assess the existence of low-lying excited states that might aid the dissociation of H$_2$. The results are shown in Figure 4.2d. Because of the nearly free-electron character of Al, a plethora of excited states exists with very low excitation energies. Along the reaction pathway, frequent state crossings and strong couplings are to be expected. This characteristic property of Al hinders the determination of specific reaction barriers for different excited states, as was possible for the dissociation of H$_2$ on Au nanoparticles. Nevertheless, a variety of different reaction pathways can exist along these excited state potential energy surfaces, some of which can be expected to be lower than in the ground state. The low-lying excited states offer possibilities for enhancement of the reactivity, consistent with a significant contribution from interband transitions in addition to plasmons, as seen in the experiment.
Chapter 5

Summary

On the basis of the combined experimental and theoretical results, we suggest a similar though not identical reaction mechanism to that proposed for H₂ dissociation on Au in an earlier study. Hot electrons formed by either the interband transition or decay of the plasmon excitation can further increase the CT already seen in the ground state and lead to an even stronger population of the hydrogen antibonding orbital. Hot electrons formed by excitation of the interband transition are able to contribute to this process due to their relatively high energy in Al. Moreover, Al features a large number of low-lying excited states because of its distinct nearly free-electron character. The formation of such a transient negative ion state is stabilized by its image potential in the metal. Its lifetime can be sufficiently long on small Al NCs to allow for an elongation of the hydrogen bond length along the PES of an excited CT state before the electron is returned to the metal surface. Depending on how far the dissociation has proceeded by this stage, it can be completed either in the excited or the ground state, or the molecule relaxes back to its equilibrium ground state structure.
The first use of Al NCs as a photocatalyst for hydrogen dissociation is demonstrated in this thesis. First-principles quantum mechanics calculations support a mechanism based on hot electron transfer from Al NCs to hydrogen molecules, populating their antibonding orbitals and weakening the H−H bond. In addition to the well-recognized role of surface plasmon decay as an origin of hot electrons, the interband transitions of Al also yield hot electrons energetic enough to facilitate this reaction. This unique feature of Al NCs is of great interest in manipulating chemical reactions using photons with different energies.


