# High Throughput Catalyst Screening via Surface Plasmon Spectroscopy

**Authors:** Professor Paul Mulvaney

**Performing Organization:** University of Melbourne

**Sponsoring Agency:** AOARD

**Abstract:**
The overall goal of this research was to utilize rapid surface plasmon spectroscopy to develop a new platform to correlate catalytic performance and behavior with catalyst morphology (e.g., size, shape) of individual core/shell nanoparticles. Kinetic experiments were performed on dihydrogen adsorption, but the findings are expected to be generally relevant to other surface-critical heterogeneous chemistries. Comparative studies of Au/TiO$_2$/Pt, Au/ZnO/Pt, Au/SiO$_2$/Pt were done to evaluate the spectroscopic methodology. It was found that substrate choice was critical to hydrogen adsorption and that hydrogen does not dissociate on gold nanoparticles on TiO$_2$ in N$_2$:H$_2$ mixtures, but does dissociate in air:H$_2$ mixtures. In the presence of Pt, dissociation occurs on Pt, and in the presence of a semiconducting matrix H$_2$ spillover occurs with electrons able to migrate to the gold particles. High-throughput combinatorial screening was used to create catalyst libraries by fabricating nanoarrays (20nm features) of individual nanocrystals using Capillary Force Assembly. Active research is focused on studying electron-transfer during catalysis to show that this methodology can distinguish between different individual catalysts in the array at the single nanocrystal level.

**Subject Terms:** Catalysis, Spectroscopic Techniques, nanoparticles, Morphological characterization, Defects
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“High Throughput Spectroscopic Catalyst Screening by Surface Plasmon Spectroscopy”

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PI information: Paul Mulvaney; mulvaney@unimelb.edu.au; University of Melbourne; School of Chemistry & Bio21 Institute; Level 2 Nth, 30 Flemington Rd., Parkville, VIC., 3010, Victoria Australia, Tel: +61 3 8344 2405; Fax: +61 3 93481595.


Specific Aims from original AOARD Application:
• Develop a new experimental technique for studying important chemical reactions such as CO oxidation, H2 production and other surface catalysed reactions.
• Provide experimental proof that catalysis can be monitored at the single particle level.
• Prove that spectroscopy can provide fast reliable screening of catalysts at the ensemble and single particle level.
• Provide evidence that SPS can be used to identify the key facets in important catalytic reactions. This data can be directly correlated to DFT calculations of the binding energies of substrates such as CO, O2 and CO2 to different crystal facets.

Abstract:
Why the work was done: Catalysts play an essential role in commercial chemistry, contributing directly to some 75% of all products in the petroleum industry and generating some $900 billion dollars in products annually around the world, while employing (in 1990) 750,000 workers. In the longer term, breakthroughs in catalysis are essential for solving several global problems. For example, to alleviate long-term climate change, catalysts for CO2 reduction are needed, while cheaper ammonia through catalytic N2 fixation offers cheaper fertilisers. Furthermore 70% of human energy consumption is in the form of fossil fuels, and in order to meet renewable energy targets, cheap catalysts for solar driven water splitting into hydrogen and oxygen are required.

Central to all these global challenges is the need for better understanding of how catalysts work. In this 1-year study, we have developed a new platform for studying catalysts spectroscopically. The goals are to show that catalysts undergo spectroscopic changes during reactions that allow new insights into how they work. We are also working on methods to enable this technique to enable high throughput testing of catalysts.

What was accomplished: In the 12 month period, we have:
(i) Constructed a new spectroscopic method for studying electron transfer during catalysis and shown that this spectroscopic method can distinguish different catalysts. We also find we can directly investigate the role of different support materials.
(ii) Created a nanofabrication method to allow us to create a library of single nanoparticles so that we can investigate the catalytic efficiency of materials at the single nanocrystal level.

Background & Concept:
A heterogeneous redox catalyst can be envisaged to work as follows. The reducing agent adsorbs to the catalyst, and usually it dissociates, which leads to formation of reactive surface intermediates.
Electrons are transferred from the intermediates to the metal, which can store large numbers of charges. These are picked up by the oxidant leading to reduction. Key questions in catalysis are always: (i) what is the best metal (ii) what role does the matrix play (iii) how are charged species stabilized?

Scheme 1: Redox catalysis involves electron exchange or transfer from a donor D- to an acceptor A. The metal accelerates the chemical reaction by allowing large numbers of electrons to collect, acting like an “electron pool”. In “real” reactions, protons are always intricately involved and the reaction is usually a multiple H atom transfer from DH₂ to A. Understanding where the protons reside and how coupled transfer of protons and electrons proceeds is at the heart of redox catalysis.

In normal catalysis, the focus is on measuring the global rates of reaction as a function of the reactant concentration and products are analysed by GC etc. However this provides little insight into the mechanism. By looking at changes in catalyst charge, we aim to uncover more details about mechanisms. In Scheme 1, we highlight how simple redox catalysis works. The first question is, does a reductant transfer electrons to the catalyst even when the acceptor is not present? Because we can see the catalyst particle accumulating or losing charge, we can simplify the redox chemistry: By exposing the catalyst just to the reductant D- (in this case H₂ or CO), we can see the “half-cell” reaction:

\[ \text{D}^- + \text{Catalyst} \rightleftharpoons \text{D} + (\text{Catalyst})^- \]

In this AOARD project we found that we can clearly see large differences, depending on whether there is oxygen or nitrogen present, the nature of the substrate and the presence of other catalyst particles in the system.

Experiment:
I. Instrumental Set-Up: AOARD funds were used primarily to purchase a new Princeton Instruments Isoplane spectrometer with improved optics for the dark field system. This new instrument enables broad spectra to be collected faster, with higher wavelength resolution and without manual stitching. Our spectroscopy system was also modified to enable gas studies.
Scheme 1: A dark field spectroscopy set-up was constructed with a home-built fluid cell so that we can study the optical properties of single catalyst particles in the presence of different gases. Left: The experimental set-up. Light from either a mercury lamp or from a halogen lamp illuminates the microscope slide through a dark field condenser. Light scattered by single particles is collected by a spectrometer and into a CCD. Bottom right: A dark field image showing a hundred or so single, well-dispersed gold nanocrystals. We use a FIB to mark the microscope grid (blue lines) so we can locate repeatedly the same single nanoparticle in the SEM, allowing us to compare the spectral results with morphology. Top Right: The catalysts can be dispersed onto glass or within various oxide matrices (e.g. ZnO, silica, titania) as long as they do not scatter light.

II. Preparation of Catalyst Particles and Substrates:

(a) Gold NRs, with 13±4nm diameter and 40±9nm length, were prepared according to the seed-mediated method proposed by El-Sayed, by reducing HAuCl₄ with sodium borohydride (NaBH₄) in water, in the presence of hexadecyltrimethylammonium bromide (CTAB) to obtain the seeds. A growth solution was then prepared with CTAB as templating agent for the NR growth and ascorbic acid as a mild reducing agent; the final step was the addition of 12 µL of seed solution to the growth solution at 27-30 °C. The color of the solution gradually changed within 30 min. In order to eliminate CTAB in excess the NRs has been centrifuged twice at 7000 rpm for 20 min, and redispersed in water each time. The final solution was diluted 10 times from the as-synthesized concentration.

(b) Platinum colloids with 10 nm diameter were prepared using the polyol method. A solution containing 80 mM chloroplatinic acid hydrate (H₂PtCl₆) in ethylene glycol was rapidly added to a solution of poly(vinyl pyrrolidone) (PVP) 30 mM and sodium nitrate (NaNO₃) with ratio NaNO₃/H₂PtCl₆ 9:1 in ethylene glycol, at 160 °C. Ethylene glycol serves as both the solvent and the reducing ag
ent. The NPs were dispersed in ethanol leading to a 30 mM sol.

(c) **TiO$_2$ NPs** were synthesized by adding 10.5 mmol of titanium tetraisopropoxide (Ti(OPr)$_4$) into a previously prepared solution containing water, hydrochloric acid and methanol with molar ratios H$_2$O/TiOPr=12.25, HCl/ TiOPr=1.72. The solution was stirred for 60 minutes at room temperature and then heated in an oil bath at 70 °C for four hours under reflux. Particles were then precipitated and dispersed in methanol to yield a clear TiO$_2$ anatase sol.

(d) **SiO$_2$ NPs:** A silica sol was prepared starting from tetraethyl orthosilicate (Si(OC$_2$H$_5$)$_4$, TEOS), ethanol, water and hydrochloric acid using the following molar ratios: H$_2$O/TEOS = 4, EtOH / TEOS = 2, HCl/TEOS=0.01. The solution was left to stir at room temperature for 1 hour before deposition.

### III. Sample Preparation

Samples for DFM measurements were deposited on fused silica quartz slides or silicon substrates by spin coating at 3000 rpm for 30 s and annealed for 10 min in air. The prepared samples are reported in Table 1. The bare Au NR samples (1) were prepared by spin coating the aqueous Au colloid solution at 3000 rpm for 30 s and then drying the sample at 70 °C for 10 min. The Au NRs + Pt NPs samples (2) were prepared by spin coating the Pt NPs containing ethanol solution at 3000 rpm for 30 s and dried at 150 °C. Following this, the aqueous solution of Au NRs was spin coated onto the Pt NPs monolayer in the same manner as the bare Au NR samples, and annealed at 70 °C. The Pt NPs were deposited at the bottom because they need to be annealed at a higher temperature to work effectively as a catalyst and on the other hand, the Au NRs cannot be treated at temperatures higher than 70-80 °C as they tend to spheroidize; this restriction determined the order of the layers in the case of bare NPs. This restriction was overcome by covering the NRs with the TiO$_2$ matrix, as this enables the annealing temperature to be increased up to 150°C without changes to the NR morphology. The Au NRs + TiO$_2$ samples (3) were prepared initially in the same way as the Au NR sample, with a further layer of TiO$_2$ NPs deposited at 3000 rpm for 30 s and then annealed at 150 °C for 10 min. The Au NR + (TiO$_2$-8%Pt NP) samples (4) were prepared in the same way as the previous sample, except with an ethanolic mixture of TiO$_2$ and Pt NPs in a ethanolic solution instead of just TiO$_2$. Au NR + TiO$_2$ + Pt NP samples (5) were prepared exactly as the Au NR + TiO$_2$ samples were, except before the annealing step, a sub-monolayer of Pt NPs were spin coated on the top of the sample. Finally, the Au NR + (SiO$_2$-8%Pt NP) sample (6) was prepared by spin coating the Au NR solution as for the bare Au NRs, then, the SiO$_2$ solution was mixed with the Pt NP solution, and spin coated onto the top of the
Au NR sub-monolayer. These samples were also annealed at 150 °C for 10 min.

**IV. Instrumentation:** Absorption spectra were collected with an Agilent 8453 UV-visible spectrometer, between 200-900 nm, on films deposited on glass substrates. X-ray diffraction (XRD) characterization has been performed by using a Philips PW1710 diffractometer on films deposited on Si substrates. The analyses were performed at an incident angle of 3° using CuKNi-filtered radiation at 30 kV and 40 mA. Optical constants $n$ and $k$ and films thickness were evaluated by measuring variables $\Psi$ and $\Delta$ with a J.A.Wollam V-VASE spectroscopic Ellipsometer at two angle of incidence (60° and 70°) in the wavelength range of 300-1500 nm. This data was fitted using WVASE ellipsometry software. Transmission electron microscopy (TEM) images were acquired on a FEI Technai TF20 microscope operating at 200 kV. TEM samples were prepared by drop casting the sample solutions onto copper TEM grids (300 carbon mesh) and drying in ambient conditions. Scanning electron microscopy (SEM) was performed on a FEI Nova 200 Nanolab microscope operating at 5 kV. The single-particle time-resolved measurements were performed using a Nikon TE2000-S Eclipse Inverted Microscope equipped with a Nikon dry dark-field condenser and a 40X/0.6 NA ELWD dry objective lens in transmission configuration (see Scheme 1). An Isoplane SCT 320 imaging spectrograph (Princeton Instruments) fitted with a PIXIS 1024F CCD detector was coupled to the image output of the microscope for spectroscopic measurements. The samples were placed in a custom made cell which allow scattering spectra to be collected under different environments. The measurements were taken at room temperature (RT) using 50,000 ppm H$_2$, balanced with N$_2$ or air, with a flow rate of 0.07 L/min.

**Results and Discussion:**

**I. Hydrogen Interaction with Gold Nanocrystals on Glass**

We first tested the stability of the spectroscopic system and the Isoplane spectrometer. When gold spheres or rods are exposed to nitrogen gas, the scattering spectra are found to be extremely constant. We find that the experimental peak position can be determined to better than ±1nm for minutes at a time. We use IGOR to fit the spectral peak position, intensity and FWHM numerically (see Appendix). There is little evidence for heating effects and the biggest challenge is slow drift in the focal position of the microscope. The control experiments show that surface plasmon spectroscopy of single particles in the absence of any surface chemical process provides is very stable.

In Figure 1, we show the first key results of this work. It has long been claimed that gold is a
poor catalyst for hydrogenation because it does not form stable bonds with surface H atoms. H atoms are strong reductants and if H₂ dissociates on gold, it should inject electrons leading to a blue shift in the scattering spectra. In Figure 1, we show the effect of exposing bare gold nanorods (NR) initially under dry nitrogen to 5% H₂. It can be seen that alternate injections of hydrogen and nitrogen lead to no discernible spectral changes to the catalyst. In agreement with literature, we do not see any evidence for hydrogen dissociation on gold nanocrystals.

Figure 1: Bare gold nanorods were dispersed on glass microscope slides. They were exposed to N₂ first and the spectra were found to be extremely stable. They were then exposed to cycles of N₂, followed by 5% H₂ in N₂. There was no discernible change in position, showing that H₂ does not adsorb significantly to gold rods at room temperature.

Figure 2: When a small amount of Pt nanocrystals were spin coated onto the slide, the scattering spectra from the \textit{GOLD NRs} did shift weakly to the blue, showing that the gold particles accumulated electrons under these conditions.

However, when a small concentration of platinum nanoparticles is adsorbed onto the gold particles, and the sample exposed to 5% H₂ in N₂, small clear blue-shifts are observed (Fig 2). We can explain this shift by assuming that H₂ dissociates on the Pt particles and that free electrons then migrate to the gold particles. Noble metals should act as a sink for electrons. In this case, the gold particles really act as a spectroscopic sensor, not a catalyst. They are charged only when the Pt nanocrystals are active. Our initial conclusion from this is that the literature is completely correct. Gold by itself is unable to function as a
hydrogenation catalyst. The question that arises is, do the Pt particles need to be touching the gold particles for electron transfer to occur or can the electrons be transported to the gold through the substrate?

II. Effect of TiO₂ Substrates

To determine whether electrons migrate through a substrate during catalysis or are localised to one nanocrystal, we compared three substrates: TiO₂, ZnO and SiO₂. In Figure 3 (left), we present the time dependent peak position of the gold nanorod spectrum vs time during exposure to N₂:H₂ cycles. As before, there was no discernible effect of hydrogen and we conclude that there is no adsorption of hydrogen onto gold irrespective of whether it is supported on glass or titania.

Figure 3: (Left) Plot of the surface plasmon peak of gold nanorods embedded in TiO₂ sol-gel films as a function of time during cycling with nitrogen and 5% H₂:N₂. (Right): Pt particles dispersed into the TiO₂ films.

We then introduced Pt particles into the titania solution during spin coating. An SEM of the Pt particles in the film shows they were well dispersed with a few aggregates.
Remarkably, we immediately see strong, very reversible shifts in the peak during cycling (Figure 4). There is also an increase in scattering cross section of the particles during catalysis. Typically, the peaks shift within 30sec to 1 minute of exposure. From this we conclude that only in the presence of Pt does the gold exhibit a blue-shift. It appears gold is a spectator during Pt interactions with hydrogen gas. What we see here is often termed “hydrogen spillover”. Electrons or H atoms migrate from catalytically active Pt to the gold, but it is unclear still whether the Pt particles need to be in direct contact with gold. In other words are the only gold particles picking up electrons, those in direct contact to a Pt particle? To answer this question, we need to physically isolate the Pt and gold particles and determine whether electrons still accumulate on the gold particles.

![Figure 5: Pt particles are spin-coated on top of a gold-TiO$_2$ film and exposed to H$_2$.](image)

In Figure 5, we isolated the gold nanoparticles from the Pt particles with a titania film. The gold NRs still exhibit a spectral blue-shift. This means that electrons liberated on Pt do migrate through the substrate. These results lead to the surprising conclusion that catalyst particles directly communicate with each other during catalysis. Electrons flow from metal particle to metal particle through the substrate, at least for titania, a semiconductor, widely used in catalysis.

\[
2H^+ + O^{2-} \rightarrow H_2O
\]

Distribution A: Approved for public release. Distribution is unlimited.
III. Role of the Substrate: We also compared spin coated sol-gel films of ZnO and SiO₂ to determine how important the carrier substrate is.

The crucial role of the substrate is apparent from the results in Figure 6. Silica is a poor substrate for hydrogen dissociation. No shifts are observed even when Pt particles are embedded in the silica. However Au NRs embedded in ZnO containing Pt particles do exhibit a blue-shift, although they are inert in the absence of Pt. This demonstrates that the substrate needs to be semi-conducting. Insulating oxides such as SiO₂ cannot facilitate electron transfer from the Pt to gold particles. Below we pictorially summarise how we have tried to use surface plasmon spectroscopy to study H₂ interactions with gold particles.

Most importantly from this part of the study, we find that the substrate is crucial and that electrons migrate through the substrate. We do not know how much of the hydrogen on Pt dissociates into free electrons and how much remains as H atoms on the Pt surface. An important trend is shown in Figure 7 below. When Pt particles are adsorbed directly onto the gold NRs, the shifts are smaller than when they are dispersed into an overlying TiO₂ substrate. There is a faster and more extensive dissociation in the latter case. Hence, we deduce that the factor limiting the rate of H₂ dissociation is not electron transfer to the matrix but the availability of H⁺ binding sites. Only when there is a good metal oxide to
soak up the protons produced during electron injection can free electrons be generated. TiO$_2$ is a better substrate because it is a better host for protons than ZnO or SiO$_2$, which are more acidic surfaces.

![Figure 7: Comparing typical traces for the shift of the SP band of gold during catalysis leads to the conclusion that the presence of TiO$_2$ leads to faster and more extensive hydrogen dissociation. The gold here is simply acting as an indicator for the availability of free electrons in the system during hydrogen gas exposure.](image)

V. The Role of Oxygen

For most of this 1-year study, experiments were carried out on N$_2$:H$_2$ mixtures. N$_2$ was used primarily to keep out moisture and also to minimize the risks of explosion due to having O$_2$:H$_2$ mixtures in the lab. All the results so far are consistent with literature, which claim that hydrogen does not dissociate at room temperature on gold metal surfaces, even for 30nm rods and spheres. We then explored the behaviour of using air:H$_2$ mixtures rather than N$_2$:H$_2$. The results were completely unexpected.

When air was used as the reference gas, introduction of hydrogen led to blue-shifts for Gold on titania (in the absence of Pt). This was the first time we had seen clear electron accumulation on gold in the absence of Pt.
Figure 8: The role of Oxygen. When the buffer gas is switched from N₂ to air, gold nanocrystals are switched on! (Right): The gold rods now exhibit a clear and strong blue-shift upon exposure to air. We observe the first clear evidence for room temperature adsorption of hydrogen onto gold nanorod surfaces. (Left): Pt still has a pronounced role. The blue-shifts become even stronger showing that in the presence of air and Pt NCs, accumulation of electrons is even stronger on the gold catalyst surfaces.

The role of oxygen is surprising. Why would electron transfer to gold be enhanced by an oxidant, which removes electrons from the noble metal surface?

The clue lies in the fact that again, gold nanorods show no shift in air when adsorbed to silica substrates. This suggests that it is the interaction of oxygen with the TiO₂ which is critical. We deduce that oxygen creates proton acceptor sites on TiO₂. In order to dissociate into electrons and protons, the protons must also adsorb to the catalyst surface. Oxide ions on the surface play a crucial role. Protons bind to surface oxides and form water, releasing electrons into the substrate.

$$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- + \text{O}^2- (\text{ads}) \rightarrow \text{H}_2\text{O} + 2\text{e}^-$$
The capacity of the substrate to soak up protons determines the amount of H₂ dissociation and electron harvesting by the gold surface. We still cannot determine whether the H₂ dissociates on the gold, with the protons migrating to nearby TiO₂, or whether the H₂ dissociates onto the TiO₂ itself with free electrons wandering through the TiO₂ and simply being trapped on the gold particles.

Below we summarize the way we have tried to uncover the interactions of hydrogen with gold nanocrystal surfaces. We believe the results here demonstrate that surface plasmon spectroscopy offers an important new technique for probing the mechanisms involved in redox catalysis.

**Matrix Effects:**
Table 1- The order of the layers and the material composition for the six different samples prepared for optical measurements, in red the Au NRs, in black the Pt NPs, in gray the TiO₂ matrix and in blue the SiO₂ matrix.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Au NRs</td>
</tr>
<tr>
<td>2</td>
<td>Au NRs + Pt NPs on glass</td>
</tr>
<tr>
<td>3</td>
<td>Au NRs + TiO₂ on glass</td>
</tr>
<tr>
<td>4</td>
<td>Au NRs + (TiO₂-8%Pt NPs) on glass</td>
</tr>
<tr>
<td>5</td>
<td>Au NRs + TiO₂ + Pt NPs on glass</td>
</tr>
<tr>
<td>6</td>
<td>Au NRs + (SiO₂-8%Pt NPs) on glass</td>
</tr>
</tbody>
</table>

**Summary Part I.**
Using hydrogen adsorption as a simple system, we have shown that:

- Gold particles interact strongly with the environment and substrate. The best system is gold and titania, gold on ZnO works less effectively, while gold on silica does not function as a catalyst.

- Hydrogen does not dissociate on gold nanoparticles on TiO₂ in N₂:H₂ mixtures. However, it does dissociate in air:H₂ mixtures.

- In the presence of Pt, dissociation occurs on Pt and in the presence of a semiconducting matrix, H₂ spillover occurs with electrons able to migrate to the gold particles.
Generally adsorption is reversible but equilibrium takes several minutes at room temperature. In the study to date, the results have focussed more on “yes” or “no” questions. In future studies we will attempt to do quantitative studies of adsorption kinetics etc.

We will then shift to looking at CO, for which gold is a known catalyst and try to see if morphology differences can be discerned.

II. Fabricating Arrays for High Throughput Analysis

The second part of our program has been the design of nanofabricated arrays to streamline and accelerate optimization of catalysts. We use a combination of nanofabrication to produce PMMA templates with customized cavities of various shapes and sizes (see Figure 9). We then introduce a heterogeneous mixture of gold nanoparticles with different morphologies and use Capillary Force Assembly (CFA) to push indiviudal particles into the array (see Figure 10). The array allows us to automate the study of catalysis and to address and locate or re-locate the same particle multiple times. The hope is that we will see differences in the spectra as we expose these arrays to different reactants. This work is ongoing.

Figure 9: Nanofabrication route for printing 20nm features on silicon wafers for assembly of single metal nanoparticles.

1. Spin coat PMMA onto Si wafer to make 60nm layer of positive EBL resist
2. Bake at 170˚C for 5 minutes to cross-link PMMA
3. Write pattern into PMMA by electron beam lithography (1 hour processing time)
4. Remove unwanted PMMA by 90 second immersion in 1:3 solution of MBIK and IPA. Follow with IPA rinse and nitrogen blow dry. Cleave wafer into 8 x 8 mm chips for CFA-assembly.
Having metal particles in an array helps us do multiple experiments on single particles and we can always do SEM after to look for morphology changes.

It had previously been shown that gold spheres down to 50nm could be captured in these cavities using CFA. We want to extend this down to 20nm and capture a wide range of particle shapes in one array.

The major challenge has been controlling the contact angle of the nanoparticle solutions. CFA works only if the contact angle of the solution on the substrate is maintained around 45 degrees. However, the surfactants used to control the particle shape (typically a cationic surfactant such as CTAB) also reduce the contact angle and the particles do not get trapped. However removal of the surfactant leads to particle aggregation so we are working on this aspect at present.

Figure 10: (Left): SEM images of single gold particles including spheres, triangular prisms, hexagonal plates and rods in close packed PMMA cavities. For Dark Field Spectroscopy, the particles must be > 5 microns apart to stop overlap of the spectra. (Right): Optical image of well dispersed single gold particles in a PMMA array. The particles are mostly spheres with some triangular prisms and a small percentage of rods.

Summary:
Our second goal of creating arrays of assembled nanoparticles for screening is working. We have managed to create a few arrays that work as shown in Figure 10, but it is not yet routine. We have found EBL expensive and there is a lot of down time. We are working on switching to using NanoImprint Lithography (NIL). In this process a single master is used to stamp replicate array structures into a polymer. This has worked several times, although our small feature size pushes NIL to its limits. Adhesion of the Master is an issue as well as clean cavity shape. Nevertheless we feel we are close to making this a via platform for catalyst screening.
Appendix:

Figure S1: Typical scattering spectra. Using Igor, a Lorentzian fit is used to give the least squares fit to the peak position. Typical accuracy is ±0.5 nm for a 140-point spectrum. It takes about 1 minute to fit 400 such spectra and to plot the peak position vs time. However, downloading the files from the spectrometer takes much longer. Hence fits are done after the experiment, not in real time. This means we only discover flawed experiments after completion.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)</th>
<th>Refractive index n (at 632 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>42</td>
<td>1.89</td>
</tr>
<tr>
<td>SiO₂</td>
<td>100</td>
<td>1.43</td>
</tr>
</tbody>
</table>

Table S2- Thickness and refractive index values of the layers used for coating the Au NRs measured by ellipsometry. Effect of Catalysis on Refractive Index: One unexpected effect is that hydrogen incorporation into the TiO₂ matrix can alter the refractive index of the substrate. This effect can on its own give rise to a small spectral shift in the surface plasmon resonance. However, simulations with the data below show this cannot account for the observations we see.
Figure S2: Refractive index ($n$) and extinction coefficient ($k$) of TiO$_2$ film in N$_2$ and in H$_2$ balanced with N$_2$ (a) and in air and in H$_2$ balanced with air (b).

**Publications:**

The major part of this work will be submitted as:


3. PI Mulvaney presented some of this work at an invied talk at the ACS Conference in Dallas in March 2014 and also to groups at University of San Antonio, TX.