Light Induced Particle Coarsening of Metal Nanoparticles

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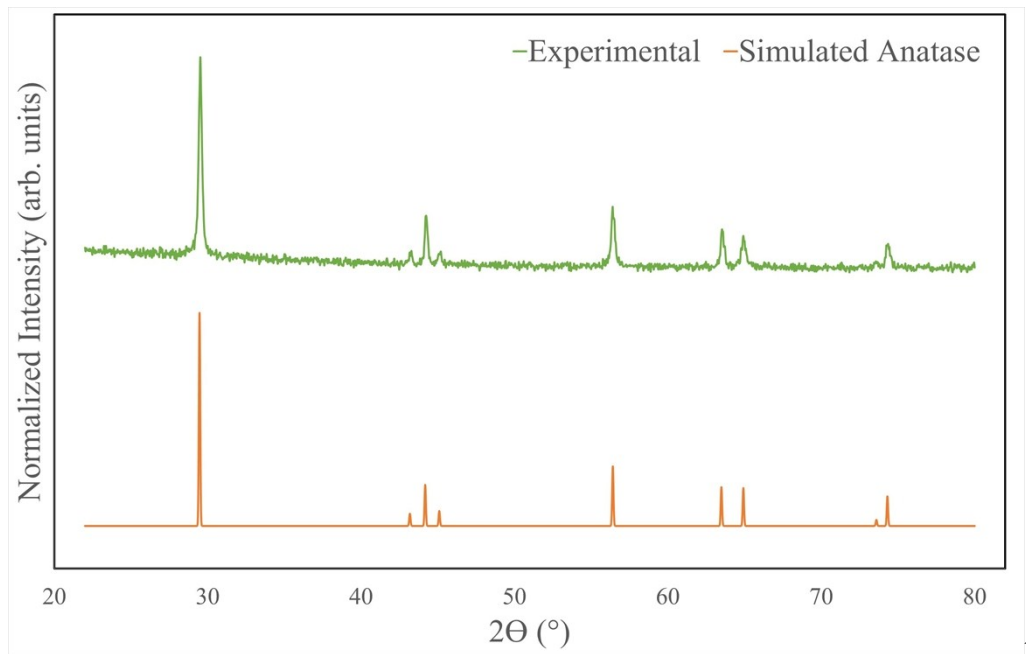Tel: 480 965 2934
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Supplemental Materials:

X-Ray Diffraction from Pt/TiO$_2$ catalysts

Fig. S1. X-Ray diffraction from catalysts sample. Upper curve is experiment and lower simulated spectrum from anatase show a good match. Pt particle signal is not detectable in the spectrum.

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In-situ TEM Characterization in Vapor H_2O

In situ TEM experiments were performed on the same samples to look for evidence of ripening in the presence of water vapor and light. An *in-situ* characterization of this Pt/TiO_2 sample in 17 Torr H_2O vapor under prolonged light irradiation was conducted in our ETEM FEI Tecnai F20 fitted with a light irradiation system [1, 2]. Typical low-dose images showing the same area of the catalyst before and after exposure to water and light are given in **Fig. S1**. There was very little difference in the average particle size even after 11 hrs light exposure. The very small changes are consistent with a small tilt in the TiO2 particle which often takes place during prolonged exposure. The coarsening was not observed presumably because vapor phase H_2O cannot provide the kinetic pathway for Pt^{2+} to be transferred from small Pt to large Pt particles. This rules out surface diffusion on TiO_2 and related transport processes in the coarsening mechanism: presumably Pt surface diffusion is slow in comparison to dissolution/deposition.
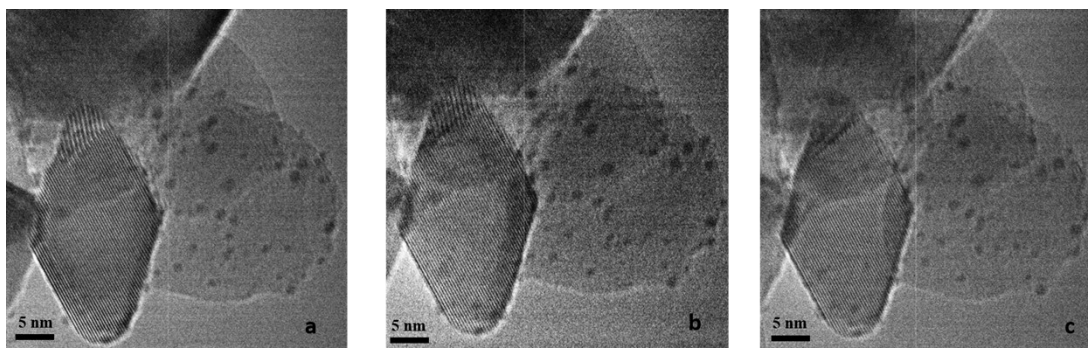
Supplement: Correlating Pt Particle Ripening with Photocatalytic Reaction Rates

Fig. S2. TEM images from *in-situ* ETEM experiments: a) fresh material; b) after 5hrs light exposure in 17 Torr H_2O vapor; c) after 11 hrs light exposure in 17 Torr H_2O vapor. Very little coarsening was observed with *in-situ* experiment in H_2O vapor.

The photoinduced particle coarsening can be related to the drop in catalytic activity observed in **Fig.** 1b. There are many possible mechanisms by which the change in particle size affects activity including: changes in Pt surface area, changes in the <u>potential of the electrons on the nanoparticle surface, changes in the areal density of Pt particles after ripening and changes in the shadowing of the TiO$_2$ by the Pt particles</u>. We make estimates of some of these mechanism and show that they are qualitatively consistent with the observationed deactivation. We do not attempt to come to a conclusion about the relative importance of the different deactivation mechanisms.

Areal Density Change

The photoelectrons generated in the TiO$_2$ must diffuse to the Pt nanoparticles and if we assume that the probability of recombination scales with the diffusion path length, a reduction in the particle density will result in more recombination and a consequent drop in the HER. The change in areal density and diffusion length can be approximately estimated from average particle size assuming the total volume of Pt is constant. We consider a system with initial spherical particles of size r_1 and areal density n_1 evolving into a new system with particle size r_2 and areal density n_2. If we assume conservation of mass (and thus volume) then the areal density ratio can be written as

$$n_2/n_1 = (r_1/r_2)^3 \tag{S1}$$

If we assume each particle is associate with a square area of width L, then the change in the separation of the particle between the initial and final configurations can be expressed as

$$L_1/L_2 = (r_1/r_2)^{3/2} \tag{S2}$$

From Table 1 it can be seen that the initial particle size is 1.7 nm and the final size is 2.06 nm showing that the number density drops by nearly a factor of 2 and the average particle spacing increases by about 25%. If we assume that recombination linearly varies with diffusion distance then eqn(S2) puts a lower bound on the increase in recombination (since we ignore TiO$_2$ thickness

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effects) and suggests a corresponding drop of at least 25% in the HER. This combined with the 23% drop in Pt surface area could certainly explain the observed drop in HER.

We can also consider how the kinetic barrier, E_b, to transfer electrons from the metal surface to adsorbed protons to make H_2 is affected by particle size. The smaller particles have a larger negative potential shift making it easier for electrons to transfer from Pt to protons. The change in the H_2 production rate taking both surface area and potential effects into account can be quantitatively estimated as follows. The rate of electron transfer is proportional to the factor $e^{\frac{-E_b + qv}{kT}}$ where E_b is the energy barrier for electrons to transfer from a bulk Pt surface to adsorbed protons; q is the electron charge; v is the potential shift of Pt particles compared to bulk Pt (i.e. $0.226/r$, the Gibbs-Thomson term in Eq.(6)); k and T are Boltzmann's constant and temperature. For the nth particle of size r_n, the surface area will be $A_n \sim 2\pi r_n^2$ and the rate of H_2 production will be proportional to

$$Rate \propto A_n \exp(-(E_b + qv_n)/kT)$$

The rate for all particles is the sum of individual rates from each particle in the system to get a total rate of

$$\text{Total Rate} \propto \sum_{i=1,n} A_i \exp(-(E_b + qv_i)/kT) = \exp(-E_b/kT)\sum_{i=1,n} A_i \exp(-qv_i/kT)$$

Giving a rate per unit mass of

$$\text{Rate/unit mass} \propto \frac{\exp(-E_b/kT)\sum\limits_{i=1,n} A_i \exp(-qv_i/kT)}{\rho\sum\limits_{i=1,n} V_i}$$

where V_i is the volume of the ith particle with density, ρ. The ratio of the rates for two different particle size distributions (summing over i and j) can now be compared and the terms involve E_b and the density, ρ, cancel giving.

$$\text{Relative rate/unit mass} \propto \left. \frac{\displaystyle\sum_{i=1,n} A_i \exp(-qv_i / kT)}{\displaystyle\sum_{i=1,n} V_i} \middle/ \frac{\displaystyle\sum_{j=1,m} A_j \exp(-qv_j / kT)}{\displaystyle\sum_{j=1,m} V_j} \right.$$

This can be evaluated from the particle size and potential distributions (**Fig** 3 and 5).

Fig. S1 shows the relative change in the H_2 production rate predicted from this equation using the experimentally determined particles size distributions. The change between the start and 180 mins does not match the experimental observation because the model does not take the transient behaviors in account. However, the model predicts a drop of around 40% in H_2 production between 180 and 550 mins which is in reasonable agreement with experimentally observed drop of about 50%. This suggests that most of the deactivation taking place in the catalyst is the result of photo-induced Ostwald ripening of Pt nanoparticles.
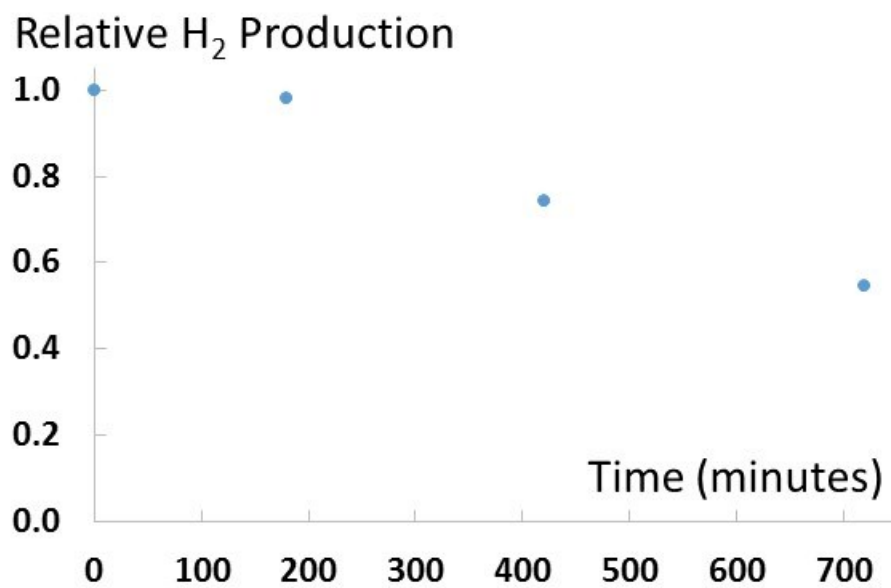
Fig. S3. Relative H_2 production as a function of time using the particle size histograms of **Fig.** 3 and 5.

1.   L. X. Zhang, B. K. Miller and P. A. Crozier, *Nano Letters*, 2013, **13**, 679-684.
2.   B. K. Miller and P. A. Crozier, *Microscopy and Microanalysis* 2013, **19**, 461-469.