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In-situ Characterization of Light Induced Ag Particle Nucleation and Growth on Anatase

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TiO_2 is a semiconducting oxide used as a UV-light photocatalyst with potential applications to degradation of organics and solar fuel generation. The photocatalytic activity can be significantly enhanced via the deposition of metal particles onto the oxide surface. Photogenerated electrons are transferred to the metal while the holes remain in the TiO_2 valence band thus suppressing electron-hole pair recombination. These materials are often prepared using photoreduction methods under light exposure during which photoelectrons from the semiconductor reduce an aqueous precursor forming metal nanoparticles. We have undertaken a series of *in situ* experiments to develop a fundamental understanding of metal particle nucleation, growth and coarsening on the surface of the semiconductors during light exposure. Such an analysis can be performed under *in situ* conditions in the presence of light and reactants in an environmental transmission electron microscope (ETEM) [1]. Here we employ a modified ETEM with a broadband light source to study the behavior of metal particles on anatase semiconductor surfaces under photoreaction conditions. Insights from these experiments can help in the design of photocatalysts with better performance and stability. We choose Ag/TiO_2 for this study because it is a good photocatalyst with a possible surface electric field enhancement by plasmon resonances on surfaces of metallic silver particles [2].

TEM samples were prepared by dipping the lacey carbon TEM grids into anatase particles suspended in $AgNO_3$ solution after 2 mins UV exposure. This provides anatase particles coated with an Ag precursor layer. *In situ* analysis is performed on a FEI Tecnai F20 ETEM operated at 200kV. The microscope was modified to allow samples to be illuminated with light from a broadband laser driven light source (EQ-99, Energetiq Technology, Inc.) with an intensity up to 10 suns [3].

The system is sensitive to electron irradiation so preliminary experiments were performed to characterize the change during exposure to the electron beam. Figure 1 shows the sample before and after 3 minutes exposure to an electron beam (but no light) with a fluence rate of $150e^-/Å^2.s$. After exposure, many particles 2 nm in size were uniformly nucleated on the substrate. Thus to eliminate the influence of the electron beam during light exposure, areas not previously exposed to the electron beam were monitored. Figure 2a shows low-dose images of fresh areas which were not previously exposed to the electron beam after 16 hrs light exposure in vacuum and Figure 2b after 18 hrs in water and light. With up to 16 hours light exposure in vacuum, very few particles were formed by photoreduction. However, many particles nucleated under light exposure when water was present. Particle formation during electron irradiation was independent of the gas environment and was probably caused by secondary electron emission from the surface during primary electron irradiation. With light exposure, excited electrons from TiO_2 cause reduction of the Ag precursor. We saw almost no photoreduction in vacuum possibly due to the high electron-hole pair recombination rate. In a water atmosphere, significant photoreduction occurs possibly because the water acts as a hole scavenger making it easier for the photoelectrons to form Ag particles. Metal particle motion and coarsening with longer light exposures will also be discussed [4].

References:
[1] Cavalca, F *et al*, Nanotechnology 2012 **23**, 075705.
[2] Zhao, G.; Kozuka, H.; Yoko, T. Thin Solid Films 1996 **227**, 147.
[3] Miller, B.K.; Crozier, P.A. Microscopy and Microanalysis, 2013 DOI: 10.1017/S1431927612014122.
[4] The support from US Department of Energy (DE-SC0004954) and the use of ETEM at John M. Cowley Center for HR Microscopy at Arizona State University is gratefully acknowledged.

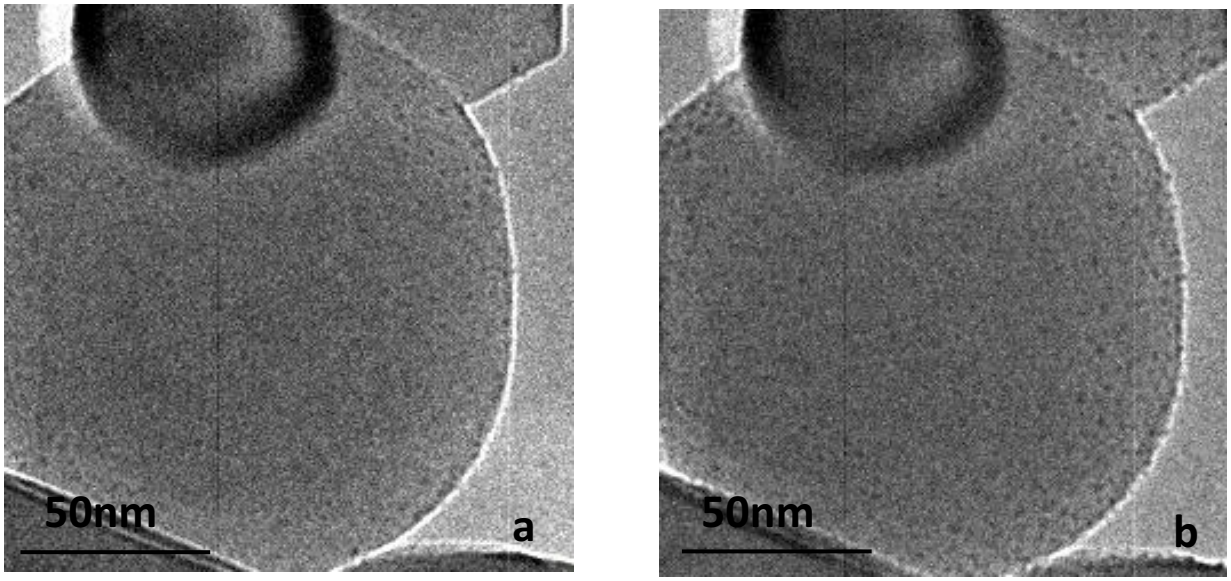

Figure 1. a) Initial Ag precursor on anatase particles. b) After 3 mins in electron beam irradiation.

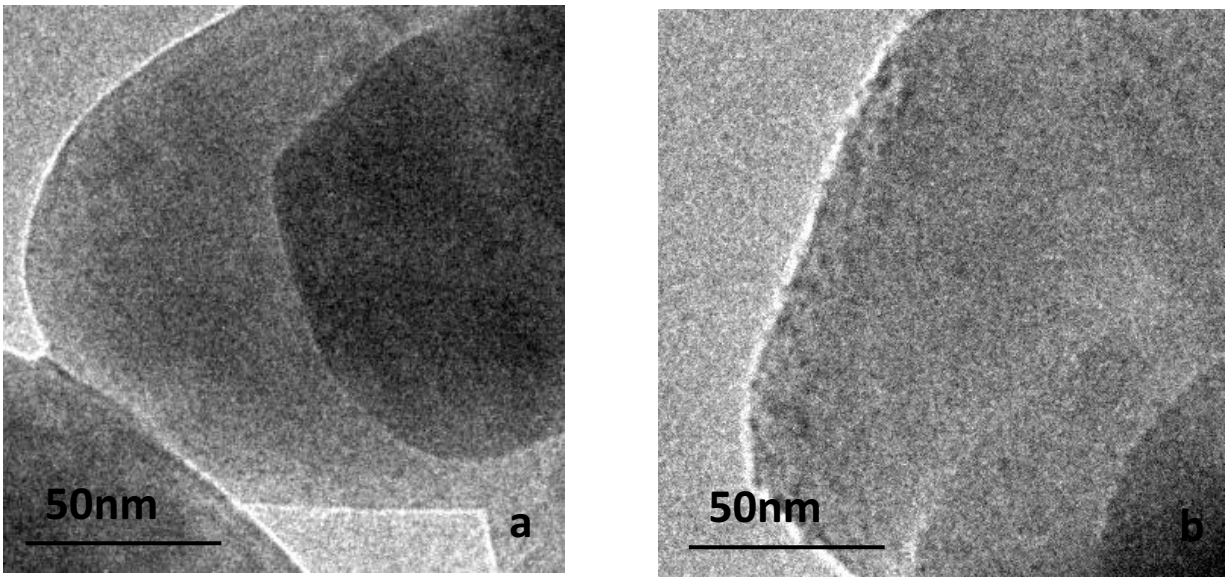

Figure 2. a) Ag precursor on anatase particles after 16hrs light exposure in vacuum. b) Ag particles on anatase after 18hrs to water and light.

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