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Atomic Level *In-situ* Characterization of Metal/TiO_2 Photocatalysts under Light Irradiation in Water Vapor

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Photocatalysts are important for environmental cleanup of undesirable organic compounds and have potential applications for solar fuel generation either through water splitting or CO_2 reduction [1]. Metal particle co-catalysts such as Pt are coupled to the semiconductor to provide chemically active sites and attract excited electrons preventing charge recombination and thus significantly enhanced photocatalytic activities. It is now recognized that atomic level *in situ* observations of catalytic materials are critical for understanding the structure-reactivity in catalysts. For photocatalysts, this requires that the system be observed not only in the presence of reactant and product species but also during *in-situ* light illumination. TiO_2 is a promising photocatalyst used for self-cleaning, pollutants degradation and water splitting etc. and has attracted intense research interest for decades since photo-decomposition of water by TiO_2 was discovered [2]. The TiO_2 photocatalysts are either anatase or rutile which has been well known. Herein we use TiO_2 as a model material to develop *in situ* photocatalytic experimental methodology and explore structure changes of metal/semiconductor photocatalysts. Such analysis can be performed under *in situ* conditions in the presence of light and reactants in an environmental transmission electron microscope (ETEM). Here we employ a modified ETEM with a broadband light source to study the behavior of metal particles on TiO_2 semiconductor surfaces under photoreaction conditions. Insights from these experiments can help in the design of photocatalysts with better performance and stability.

Well defined anatase nanobars were prepared following a hydrothermal method. Metal co-catalysts such as Pt, Ag and Cu were loaded onto the anatase nanobars using methods such as dry impregnation, photo-deposition and sputtering. *Ex-situ* experiments were performed to achieve preliminary observations under exposure to a 450W xenon lamp with a mirror reflecting 360nm to 460nm light. TEM images for *ex-situ* experiments were taken from an FEI aberration corrected Titan TEM. An FEI Tecnai F20 ETEM was modified to allow samples to be illuminated with light with an intensity up to 10 suns [3]. *In situ* analysis was performed tracking structure changes in photocatalytic vapor phase water splitting reactions.

5% wt Pt particles were loaded onto anatase nanoparticles and well dispersed through proper heat treatment. Examination of TiO_2 nanoparticles suggests Pt particles are less likely to nucleate on smooth anatase (101) planes and prefer to grow on roughened surfaces or corners. Initial Pt particle size averaged 1-2 nm (Figure 1a). Figure 1b also shows some surface roughening for the as reduced Pt on TiO_2 materials. After exposure to light in liquid water for 6hrs, Pt particles show significant sintering as shown in Figure 1c. The average Pt particle size increases to 4-5 nm. Previously we have observed surface disordering on pure anatase particles in the presence of water and light [4]. However, this Pt/TiO_2 sample shows much more significant surface disorder (Figure 2d) probably because Pt enhances the H2 evolution leaving holes to generate more oxygen vacancies which destabilizes the surface structure. *In-situ* experiments were performed to study the evolution of the Pt sintering, TiO_2 surface roughening and the Pt/TiO_2 interface changes. Other metal co-catalysts will also be discussed in the presentation.

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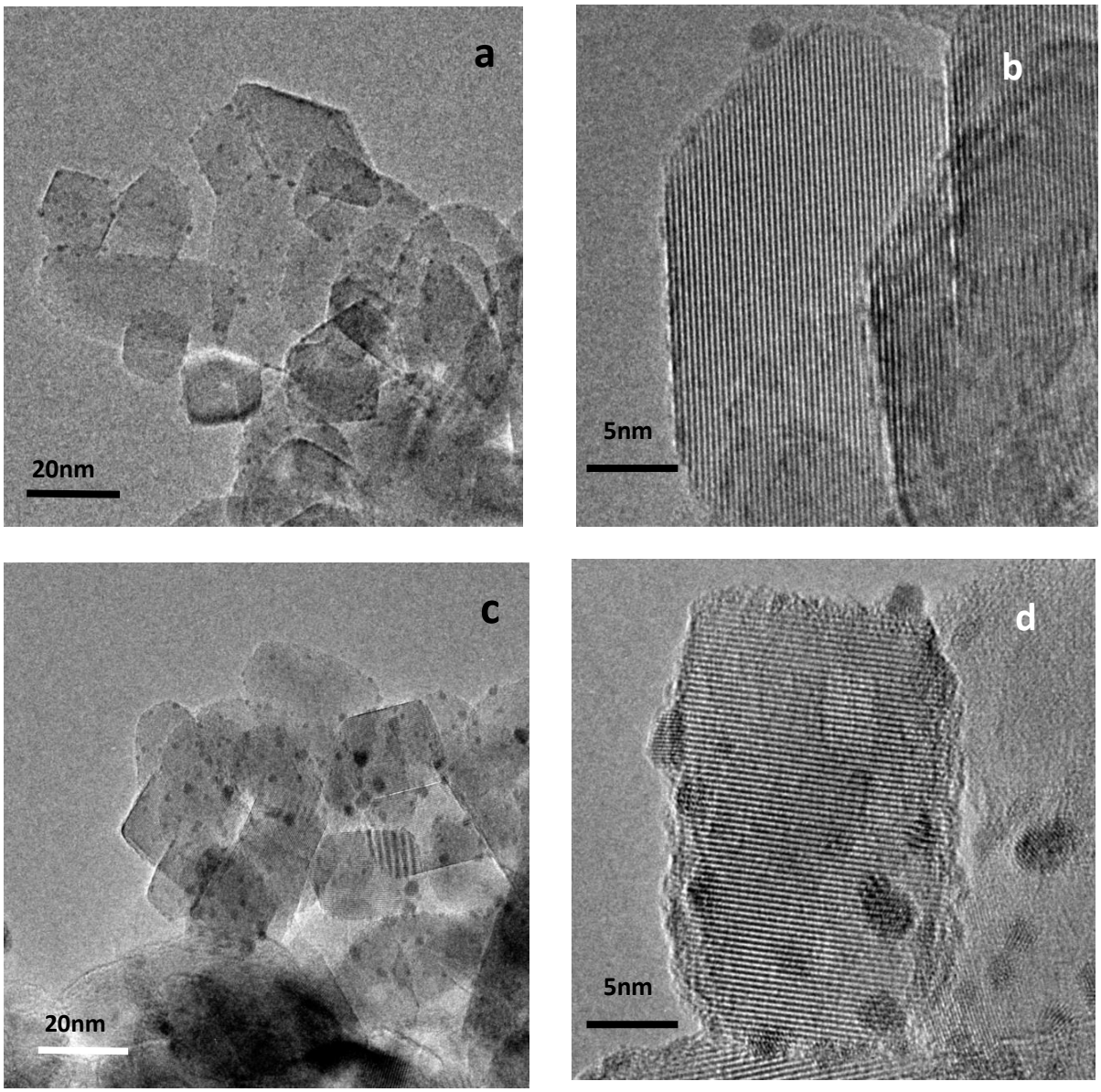

Figure 1 a) Initial 5%wt Pt on anatase particles, b) high mag initial 5%wt Pt on anatase, c)after *ex-situ* 6hrs exposure to 360nm-460nm light in liquid water, d) high mag after expsosure.

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