

Atomic Level *In-situ* Characterization of NiO-TiO₂ Photocatalysts under Light Irradiation in Water Vapor

Liuxian Zhang¹ and Peter A. Crozier¹

¹School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ, USA

Photocatalysts are important for environmental cleanup of undesirable organic compounds and have potential applications for solar fuel generation either through water splitting or CO₂ reduction [1]. 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. NiO loaded semiconductor photocatalyst with Ni first reduced and then partially re-oxidized at the surface has been reported to have good photocatalytic properties by forming a metallic Ni Ohmic contact between NiO and the semiconductors. NiO-Ni-SrTiO₃ performs better than NiO/SrTiO₃ while Ni/SrTiO₃ does not have high photocatalytic activity [2]. TiO₂ is a promising photocatalyst which has attracted intense research interest for decades since photo-decomposition of water by TiO₂ was discovered [3]. The TiO₂ photocatalysts are either anatase or rutile which has been well known. Herein we use TiO₂ as a model material to develop *in situ* photocatalytic experimental methodology and explore structure changes of NiO/semiconductor photocatalysts. *In-situ* heat treatment in H₂ or O₂ is applied to prepare initially Ni/TiO₂, NiO/TiO₂ or NiO-Ni-TiO₂ materials in an environmental transmission electron microscope (ETEM). Then, without exposure to air, analysis can be performed in the same modified ETEM under *in situ* conditions in the presence of light and reactants to explore oxidation/reduction or interface changes under photocatalytic reactions. Insights from these experiments can help in the design of photocatalysts with better performance and stability.

NiO-Ni-TiO₂ was prepared using Ni(NiO₃)₂ as the precursor following impregnation, calcination, reduction and partial re-oxidation. *Ex-situ* experiments were performed to achieve preliminary observations under exposure of 450W xenon lamp with mirror reflecting 360nm to 460nm light. TEM images for *ex-situ* experiments were recorded with a FEI aberration corrected Titan TEM. Figure 1A&1B show initial Ni-NiO core-shell structures on anatase particles. The inside rounded darker particles are Ni metals with outside shells of polycrystalline NiO. After 6 hrs exposure to light in liquid water, the oxide shells become porous and the Ni metal is absent leaving a void (Figure 1C&1D). Ni may either be oxidized to NiO or dissolved into the solution during photocatalytic reactions.

In-situ heat treatment using a hot stage sample holder with H₂ or O₂ allows Ni or NiO to be prepared as the starting material for *in situ* photocatalytic experiments. An FEI Tecnai F20 ETM was modified to allow samples to be illuminated with light from a broadband laser driven light source (EQ-99, Energetiq Technology, Inc.) with the intensity up to 10 suns [4]. Changes taking place in these Ni metal and NiO structures under *in situ* light exposure in the presence of water vapor will also be discussed.

References:

- [1]. Lewis, N. S.; Nocera, D. G. *Proceedings of the National. Acad. of Sci. of the U.S.A.* 2006, **103**, (43), 15729-15735.
- [2]. Domen, K.; Kudo, A.; Onishi, T.; J. Catalysis, 1986. **102**,92-98.

[3]. Fujishima, A.; Honda, K. *Nature* 1972, **238**, 37-38

[4]. Miller, B.K.; Crozier, P.A. *Microscopy and Microanalysis* 2013, **19**, 461-469

[5]. 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.

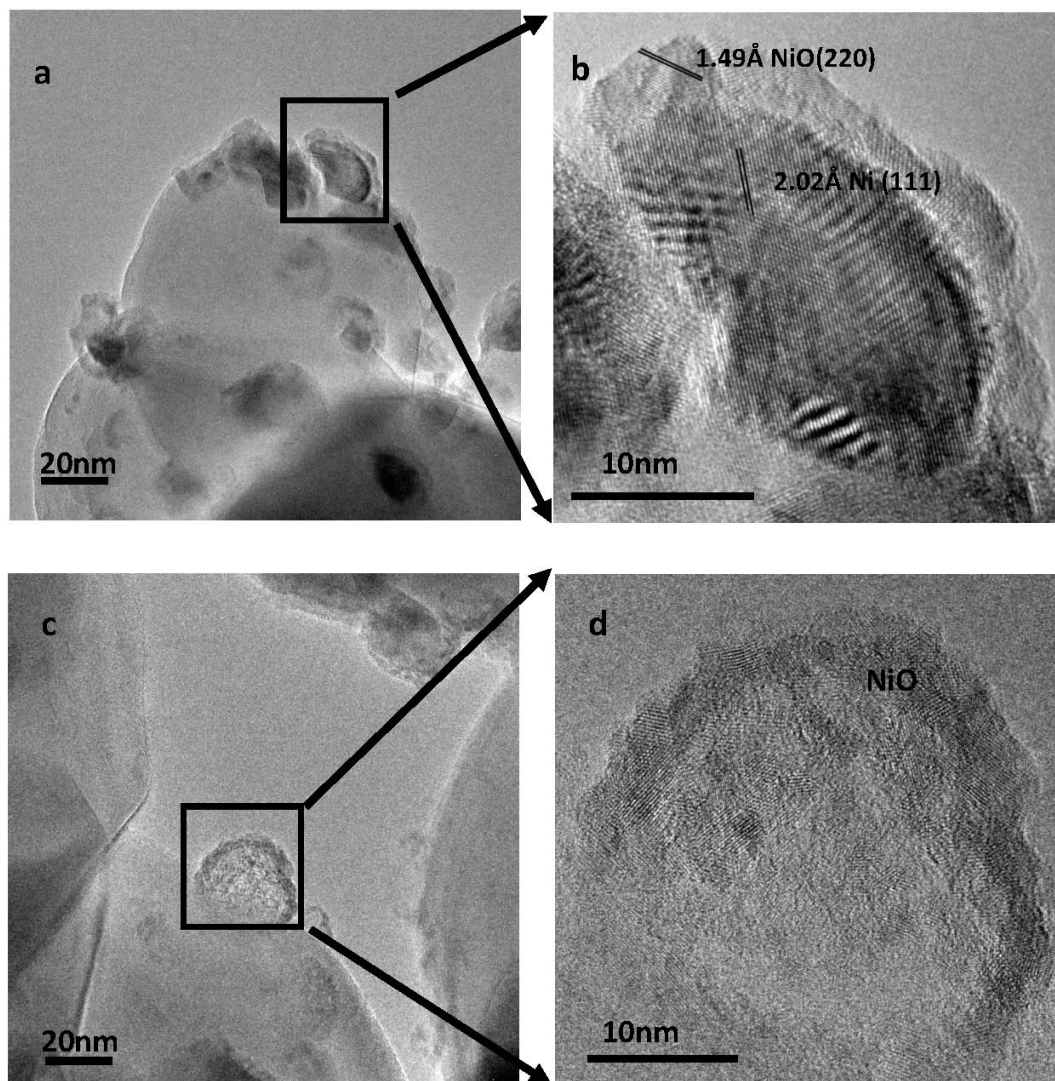


Figure 1 a) Initial 5%wt NiO on anatase particles, b) zoom in of initial NiO-Ni-TiO₂ structure, c) after *ex-situ* 6hrs exposure to 360nm-460nm light in liquid water, d) zoom in of NiO particle on anatase after exposure