

## Studying Charge Transport and Light Induced Structural Alterations in Ni/NiO Core-Shell Co-Catalysts on SrTiO<sub>3</sub> for Solar Hydrogen Evolution

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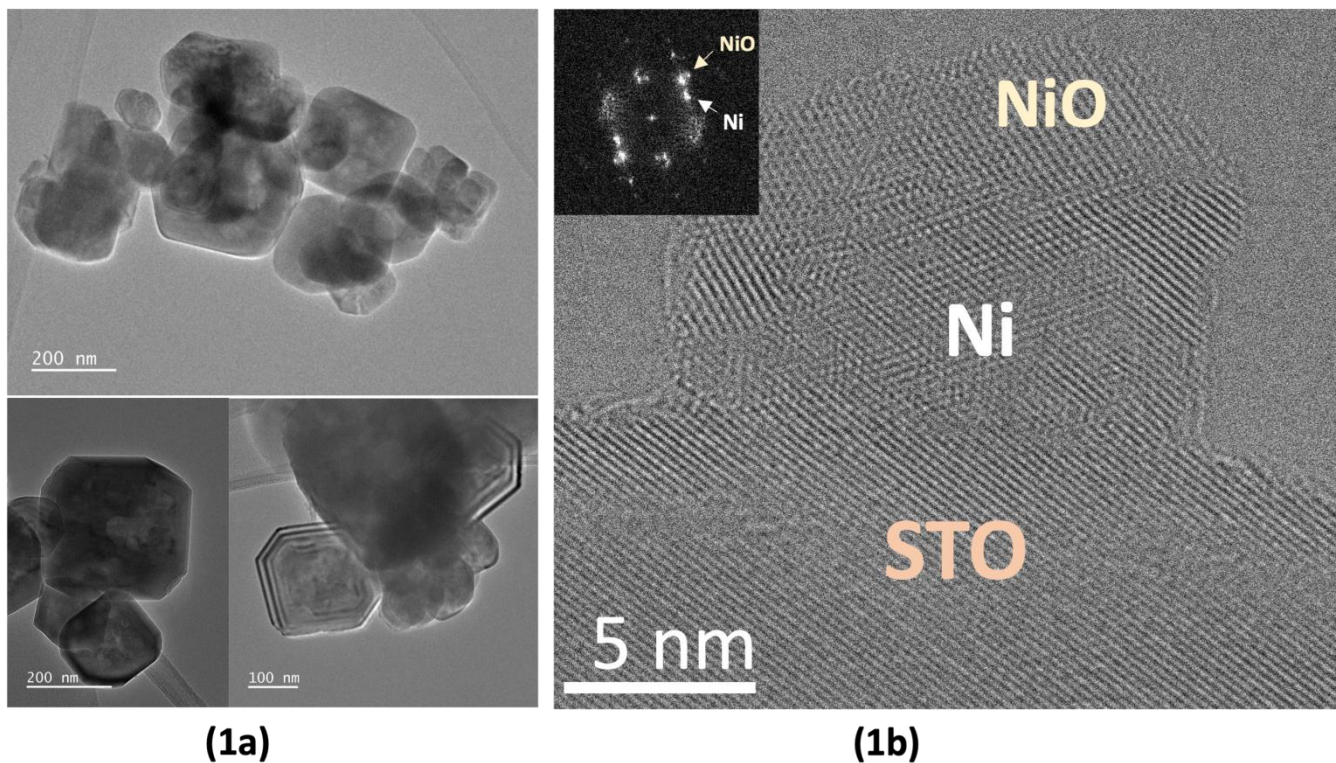
Photocatalytic water splitting offers a promising pathway for the generation of solar fuel, H<sub>2</sub>. Usually, water splitting photocatalysts are comprised of water-stable semiconductor materials (e.g., oxides, halides, sulphides, oxynitrides, etc.) that harvest incoming photons and convert them into electron-hole pairs. These charge carriers migrate to the surface and can drive the H<sub>2</sub> and O<sub>2</sub> evolution reactions under favorable thermodynamic conditions [1]. Often a co-catalyst (e.g., Ni/NiO, Pt, Au, etc.) is deposited onto the photon-harvesting semiconductor in order to enhance the reaction kinetics. The co-catalyst can offer preferential adsorption sites for the reactants and can efficiently separate the charge carriers, which prevents recombination. Structural changes during photocorrosion of a core-shell structure has been studied and suggests that Ni dissolves into solution and leaves the shell (NiO) intact thus creating a void [2]. Understanding the Ni dissolution reaction would provide an insight in charge transport across interface of co-catalyst and semiconductor substrate.

In this work, we aim to investigate charge transport and light-induced structural changes at metal/semiconductor interfaces under conditions relevant to photocatalytic water splitting. We have chosen a model photocatalyst consisting of Ni/NiO core-shell co-catalyst loaded on a SrTiO<sub>3</sub> (STO) light-harvesting semiconductor, since this type of core-shell structure loaded on semiconductor has previously shown overall water splitting [3]. Multifaceted STO cubes were synthesized using a solvothermal method reported by Wang et al. [4]. PANalyticalAeris powder X-ray Diffractometer was used for X-ray diffraction (XRD) measurements which showed peaks attributable to STO only, indicating phase purity. A 1 wt.% loading of Ni/NiO co-catalyst was deposited onto the STO substrate using dry impregnation and thermal processing methods as described by Zhang et al. in [4]. XRD did not reveal any additional peaks after impregnation. The as-synthesized and Ni/NiO-loaded STO were imaged using transmission electron microscopy (TEM) in an aberration-corrected FEI Titan TEM operated at 300 kV and equipped with a Gatan K3 direct electron detector for imaging. Photocatalytic water splitting over the Ni/NiO-loaded STO was performed with a liquid-phase photoreactor coupled to a gas chromatograph for compositional analysis of H<sub>2</sub>. A Xe arc lamp operated at 450 W was used as a light source. Methanol was used as hole scavenger; hence no oxygen was detected.

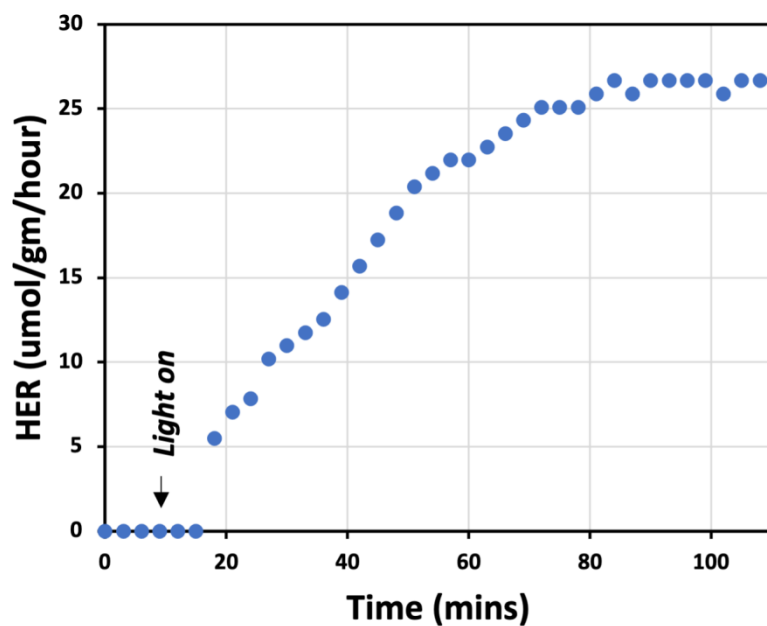
**Figure 1a** displays low magnification TEM images of the as-synthesized STO nanoparticles, which appear to have a truncated cubic shape and are roughly 100 – 300 nm in size. **Figure 1b** shows a high resolution TEM image of a typical STO-supported Ni/NiO nanoparticle observed after impregnation and processing. The HRTEM image reveals that the Ni/NiO co-catalyst consists of an oval-shaped Ni core approximately 1.8 nm in size, surrounded by a highly irregular NiO shell approximately 3 nm in width. The Ni/STO interface exhibits a high degree of coherence that can be seen by the well-aligned lattice fringes that meet at the interface. The encapsulating NiO shell is comprised of multiple domains. **Figure 2** plots the H<sub>2</sub> evolution rate (HER,  $\mu\text{mol H}_2 \text{ hr}^{-1} \text{ g}_{\text{cat}}^{-1}$ ) of the Ni/NiO-loaded STO photocatalyst as a function of time during light illumination. H<sub>2</sub> evolution was detected after 8 minutes of light illumination. We will use the structural modification caused by the Ni metal core dissolution reaction to investigate the efficiency of electron transport across the STO interface.

Although this material produces solar fuel, it is only active in the ultraviolet (UV) region of the spectrum. Since solar the spectrum constitutes ~3-5% UV as compared to the visible part which is ~42% it is important to access the visible part of the spectrum for higher efficiency. We are currently exploring the effect of Rh doping which changes the band structure and makes STO active in visible [5]. *In situ* electron microscopy

coupled with light illumination using the Thermo-Scientific Titan AC-ETEM microscope is being used to investigate the effect of light induced structural changes of the semiconductor.



**Figure 1.** Figure 1: (a) Low magnification TEM image of as-synthesized STO nanoparticles. (b) HRTEM image of Ni/NiO-STO core-shell structure. In the inset Fourier transform, spots from Ni and NiO are visible.



**Figure 2.** Figure 2: Hydrogen evolution rate as a function of time during the photoreaction of 1wt.% Ni/NiO-STO nanoparticles. Within 8 mins of light irradiation, significant hydrogen was detected as shown in the chart.

#### References

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- [6] We gratefully acknowledge support of DOE grant BES DE-SC0004954 and the use of ASU’s John M. Cowley Center for High Resolution Electron Microscopy.