

Nano-level Structure-Reactivity Relationships of Ni-NiO Core-shell Co-catalysts on Ta₂O₅ for Solar Hydrogen Production

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Tantalum oxide and many tantalate-based systems have been reported to show extraordinarily high activities and quantum yields when decomposing water under ultraviolet (UV) illumination [1]. Although pure tantalum oxide shows some photocatalytic activity, loading with a nickel-based co-catalyst improves the initial H₂ production rate by 3 orders of magnitude and results in stoichiometric decomposition of pure water into H₂ and O₂ [2]. Interestingly, this co-catalyst needs to have a particular microstructure, Ni core-NiO shell, to show high activity. However a detailed atomic-level understanding of the relationship between the catalyst microstructures and the photocatalytic reactivities has not yet been fully explored. Aberration-corrected TEM provides an efficient way to observe fine structures at this level and here we investigate the structure-reactivity relations in different co-catalysts to study both reaction and deactivation mechanisms [3].

A series of controlled Ni-NiO core-shell co-catalyst structures were prepared on a Ta₂O₅ substrate by tuning the heat treatment conditions. The photocatalytic activity of each structure was tested in pH 7 DI water in a photoreactor system interfaced to a gas chromatography (GC) for H₂ detection. An aberration-corrected FEI Titan (300 kV) was employed to study the fine difference in the initial co-catalyst structures, as well as the evolution of the materials after exposure to UV light and water.

Each initial co-catalyst sample was examined and HRTEM images were obtained. The samples varied in particle size and NiO shell thickness. Typical core-shell structures are shown in Fig 1a. Changes in the core-shell morphologies resulted in large changes in H₂ production rates and deactivation time. As is shown in Fig 1b, other than the inactive pure NiO sample, H₂ production rate first reaches a maximum value then gradually decreases over time for each active core-shell structure. The most active co-catalyst structure has a complicated morphology (Fig. 2a) with an average oxide shell thickness/particle size percentage of ~34%. It gives a maximum H₂ production rate of 189 µmol/h/g and takes about 6 h to deactivate to 50% max activity. Increased H₂ production was found to be related to an increase in the thickness of NiO shell due to suppression of the reverse reaction.

HRTEM images reveal that the core-shell co-catalyst structures deactivated primarily due to a loss of metallic Ni from the core structure. Fig. 2 shows that initially both Ni and NiO phases were present in the most active co-catalyst structure. However during deactivation, the catalyst transformed either to structures consisting of NiO nanoblocks (Fig. 2b) or hollow NiO shells (Fig. 2c). The phase transformations occurring during deactivation were associated with Ni diffusion processes that are driven by light illumination. The information we have gained by correlating microstructures with reactivities is now being employed to design improved co-catalysts structures. More analytical data to explore the chemical information will be presented.

References:

- [1] Kudo, A. and Miseki, Y., Chem. Soc. Rev. **38**, (2009) 253.
- [2] Kato, H. and Kudo, A., Chem. Phys. Lett. **295**, (1998) 487.
- [3] Liu, Q., Zhang L., Crozier P.A., Appl. Catal. B: Environ. **172**, (2015) 58.
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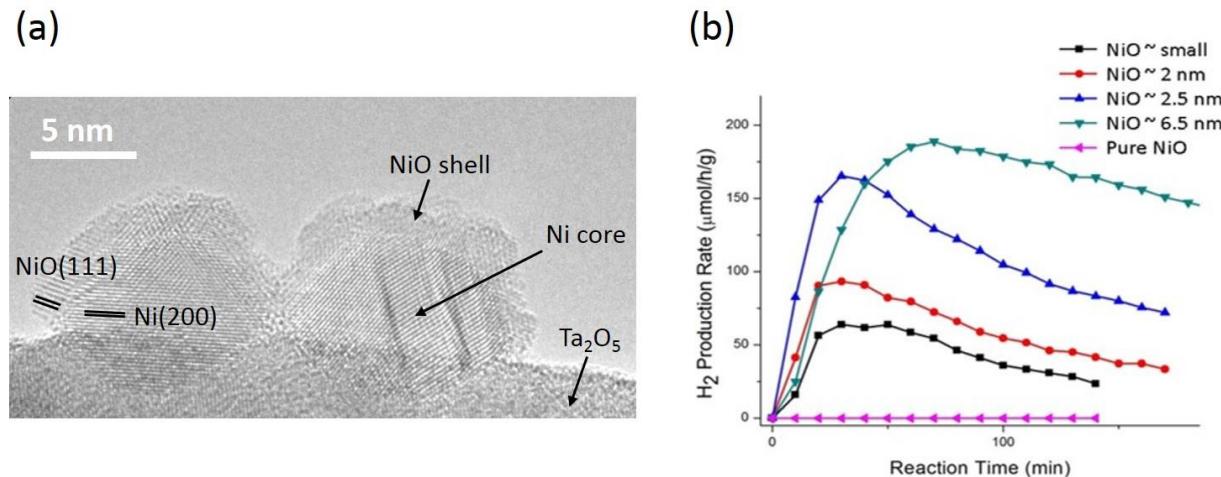


Figure 1. (a) Aberration-corrected TEM image showing a typical Ni core - NiO shell co-catalyst structure. (b) H₂ production rates vs. reaction time of different co-catalysts with a series of NiO shell thickness.

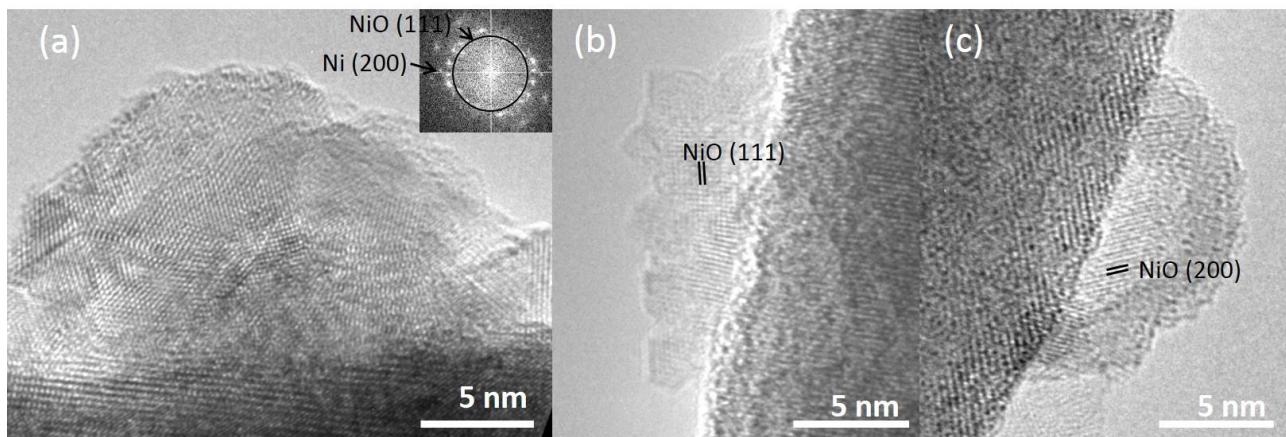


Figure 2. (a) Initial co-catalyst structure which gives the highest H₂ production. FFT indicates both Ni and NiO phases were present initially. After exposure to 16 h UV light and water, two types of deactivated structures emerge: (b) NiO nanoblocks; (c) hollow NiO shell.