Structural Evolution During Photocorrosion of Ni/NiO Core/Shell Co-Catalyst on TiO₂

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ABSTRACT: The Ni/NiO core/shell structure is one of the most efficient co-catalysts for solar water splitting when coupled with suitable semiconducting oxides. It has been shown that pretreated Ni/NiO core/shell structures are more active than pure Ni metal, pure NiO or mixed dispersion of Ni metal and NiO nanoparticles. However, Ni/NiO core/shell structures on TiO₂ are only able to generate H₂ but not O₂ in aqueous water. The nature of the hydrogen evolution reaction in these systems was investigated by correlating photochemical H₂ production with atomic resolution structure determined with aberration corrected electron microscopy. It was found that the core/shell structure plays an important role for H₂ generation but the system undergoes deactivation due to a loss of metallic Ni. During the H₂ evolution reaction, the metal core initially formed partial voids which grew and eventually all the Ni diffused out of the core-shell into solution leaving an inactive hollow NiO void structure. The H₂ evolution was generated by a photochemical reaction involving photocorrosion of Ni metal.

Introduction

Photocatalytic water splitting to produce H_2 has been considered a promising technology for generation of sustainable clean fuels. It has attracted considerable interest since water splitting was first discovered using TiO_2 as photoelectrode with external bias.¹ A water-stable oxide semiconductor is usually employed to convert photons to electron-hole (e-h) pairs for H_2 and O_2 production. However simple oxide semiconductors like TiO_2 alone are poor as photocatalysts for water splitting. The rate of water splitting can be increased by adding co-catalysts such as noble metals or coupled semiconductors.²⁻⁵ Factors such as band positions, sufficiency of reactive sites, separation of electron-hole pairs and reverse reactions have critical impacts on water-splitting efficiencies. Adding metal co-catalysts and coupling with other semiconductors can positively impact these factors by, for example, reducing e-h recombination and providing more reactive sites.⁶⁻¹¹

Among all the photocatalytical water splitting co-catalyst systems, Ni based co-catalysts have been extensively applied and shown good photocatalytical properties.¹²⁻¹⁷ It is also attractive because Ni is considerably less expensive than noble metals for water splitting and it has been extended to many different semiconductor systems like oxides of Ti, Nb and Ta photocatalysts.¹⁸⁻²⁰ Ni/NiO core-shell structure has apparently been shown to be one of the most active co-catalyst for water splitting.²¹ It's more active than pure Ni metal, pure NiO or mixed dispersion of Ni metal and NiO nanoparticles (but not in a core/shell structure).²²⁻²⁴ When first discovered, it was believed that the H_2 evolution site was NiO and the O_2 evolution site was $SrTiO_3$.²⁵ Metallic Ni was believed to facilitate electron transfer by forming an Ohmic contact between the semiconductor and NiO thus enhancing catalytical properties.²³ Following new

experiments, this mechanism was recently revised to suggest that Ni metal is the H₂ evolution site and NiO is the O₂ evolution site.²⁴

One advantage of the core-shell structure is that it may inhibit the reverse reaction from taking place by preventing oxygen from reaching the metal surface. It has been hypothesized that it is easy for protons to diffuse through the NiO shell to reach the buried interface and the metal sites where reduction can take place. H₂ can then diffuse through the NiO multi-crystal domains shell and escape. On the other hand, NiO is well known as a good barrier for O diffusion.^{26, 27} Thus the NiO shell hinders the oxygen generated during water splitting from reacting with hydrogen on the metal surface and producing H₂O. A similar mechanism is supposedly taking place in the core/shell noble-metal/Cr₂O₃ system.²⁸

To date there have been few investigations of the atomic level structure of the Ni/NiO core/shell structure and its structural and compositional evolution during the water splitting processing. This structure-reactivity information can provide insights into likely mechanisms behind the functioning of the material and also provide details on the process for deactivation. There have been reports of H₂ evolutions in pure aqueous water but no stoichiometric water splitting for NiO_x on TiO₂. O₂ evolutions were only observed with NaOH aqueous solutions or NaOH coated NiO_x/TiO₂ pretreated materials. The H₂ evolution also decreases very quickly.^{29, 30} No report has been published following the catalytic materials' structural evolutions during the reaction to explain the absence of O₂ and the drop of H₂ production. Photocorrosion is common in many of non-oxide semiconductor co-catalysts which can result in rapid deactivations. For example some sulfide semiconductors like CdS can be oxidized in photo reactions.^{31, 32} Also AgCO₃ photocatalyst undergo photocorrosion by photo reduction of Ag²⁺.³³ However no report has discussed photocorrosions of metal co-catalysts.

In this work, TiO_2 , is chosen as the model support to study the activation and deactivation of Ni/NiO core-shell co-catalyst. The system is not active for stoichiometric water splitting but the stability of the TiO_2 under water splitting conditions makes it an ideal support to use to study photocorrosion processes in the co-catalyst. Photochemical activity tests were performed under exposure to light from a xenon lamp in pure water. H_2 production was observed to drop during the reactions and no O_2 was detected. High resolution transmission electron microscope (HRTEM) images were employed to investigate the structural changes taking place in the material during de-activation. A core-shell to void-shell morphological transformation was observed to take place as hydrogen evolution declined. A simultaneous increase in the Ni^{2+} ion concentration was detected in the water as the reaction proceeded showing that photocorrosion of Ni was occurring. Analysis of the Ni ion concentration and the hydrogen evolution proves that a photochemical reaction between Ni and H_2O is primarily responsible for H_2 evolution in this case. Photo-corrosion of Ni metal and the resulting loss of Ni metal is the cause of deactivation.

2. Materials and Methods

Materials Preparation

Three different samples were prepared to give core-shell, NiO and mostly Ni metal particles on the TiO_2 support. $\text{NiO}_x/\text{TiO}_2$ was prepared with 1wt% NiO using a dry impregnation method. The calculated volume of 0.5M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.999% Sigma-Aldrich) solution was dropped onto dry commercial anatase particles (99.8% Sigma-Aldrich) with continuing milling until all the pores were saturated by solution. The mixture was dried at room temperature and calcined at 450°C in air for 3 hrs. The calcined powders were then transferred into a tube furnace and reduced in flowing 5% H_2/Ar at 500°C for 2 hrs followed by partial oxidation in 100 Torr O_2 for

1 hr at 200°C. This as-prepared material was labelled as R500-O200-TO. A second sample fully reduced in 5% H₂/Ar at 500°C but not subject to the re-oxidation step was labelled as R500-TO. A third sample was fully oxidized at 500°C in air and labelled as O500-TO.

H₂ and O₂ Evolution

0.2 g R500-O200-TO powders were suspended, stirred and sonicated in pure water in a self-designed photo reactor with a quartz window on top. A 450 W xenon lamp (Newport) with a 350-450 nm band pass mirror was used as the light source with the light coming vertically through the top of the reactor. The incident light intensity into the reactor was calculated to be about 50 mW/cm² from the manufacturer's manual and confirmed by a Si biased photo detector (THORLABS DET10A). H₂ detection was performed using a gas-chromatography (GC Varian 450, PLOT column, TCD, Ar Carrier) system connected to the photoreactor with Ar as the carrier gas continuously flowing at 5 cc/ min. Reaction products in the head space above the water were sampled every 10 minutes with the GC. The same experiments were also carried out on O500-TO and R500-TO.

TEM Characterization

High resolution TEM images were taken on an aberration corrected FEI Titan operating at 300 kV. Chemical analysis was performed using electron energy-loss spectroscopy (EELS) in an aberration corrected NION microscope operating 60 kV with 0.4 eV/channel.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The Ni²⁺ concentration in the water before and after the reactions were determined by inductively coupled plasma mass spectrometry (ICP-MS) to check if the Ni metal cores

dissolved into H₂O during the photoreaction. A DI water blank and initial samples were acidified in ~0.32 M nitric acid with trace metal grade nitric acid. A series of water samples (1ml each) were taken every 30 mins from the total volume 50ml solution during the photo-reaction over a period of 4hrs after turning on the light. The water samples were diluted five-fold to keep them within the instrument's calibration range. Samples were analyzed by quadrupole ICP-MS (ThermoFisher Scientific iCAP Q, with CCT option). Ni and Ti were run in CCT-KED ("Collision Cell Technology-Kinetic Energy Discrimination") mode with high purity He as the collision cell gas. Samples were measured at ⁵⁸Ni, ⁶⁰Ni and ⁶²Ni, ⁴⁷Ti, ⁴⁸Ti and ⁴⁹Ti, respectively to monitor for interferences, but only data from ⁶⁰Ni measurements are reported here. This isotope had the lowest detection limit and gave the most reliable and accurate Ni determination. The initial pH of the solution was 7 rising to 7.5 after the photo reaction.

Results and Discussion

Fresh Catalyst Morphology

Figure 1 shows TEM images of the as prepared Ni/NiO core/shell R500-O200-TO materials. The images show clear core-shell structures. The d-spacing of the lattice fringes gained by Fast Fourier Transformation (FFT) of the high resolution TEM images is 1.49Å at the shell which matches NiO (220) and 2.02Å at the core matching Ni (111). The FFT of the whole core-shell structure shows spots matching fcc Ni (111) , (220) and fcc NiO (111) , (200) planes. Electron energy-loss spectroscopy (EELS) line scans were performed to determine the spatially resolved elemental composition across the interfaces between TiO₂, Ni and NiO as well as confirming the core-shell structures as shown by Figure 2. A Ni L_{2,3} edge at 855 eV was observed from the shell to the core as expected in Figure 2c. An EELS line scan showing the variation in the O K-edge

intensity is also presented in Figure 2d. It shows an enhancement in the oxygen signal at the particle surface and is consistent with the projected O signal associated with a core-shell morphology. Interestingly, a Ti $L_{2,3}$ edge was also observed on the surface of the shell (Figure 2b). This is related to the strong metal-support interaction effect where in the H_2 reduction atmosphere in which the TiO_2 surface gets partially reduced by the protons from H_2 dissociation around Ni metal particles.^{34, 35} The reduced TiO_x becomes very mobile and diffuses onto the Ni metal surface and gets re-oxidized in the partial oxidation process. Apparently even after re-oxidation of Ni metal to NiO, the TiO_x remains on the outside of the NiO. The fresh R500-TO shows more rounded co-catalyst particles with fringes matching Ni metal but with a very thin layer NiO due to exposure to air.

The core-shell structured co-catalyst was uniformly dispersed among TiO_2 anatase particles with the metal particles more or less wetting the TiO_2 . The length of the contact interface between the Ni metal is defined as the contact length. The metal/semiconductor contact length and the height of the particles are similar with average values of 15 nm.

Hydrogen Evolution and Deactivation

The photo-reactivities of R500-O200-TO, O500-TO and R500-TO are shown in Figure 3. Only the Ni/NiO core-shell R500-O200-TO showed detectable H_2 evolution in these experiments. The material activated relatively quickly once light was turned on with the initial H_2 being detected after 25 minutes. The maximum H_2 production rate reached about $5.5 \mu\text{mol/hr/g}$ in about 100 minutes. This is partially explained by H_2 reaching saturation concentration, being released to the head space and then mixing fully with Ar carrier gas. After 100 minutes, the H_2 production rate started to fall as the catalyst began to deactivate with the rate dropping to about

half of the initial value after 7 hrs. O₂ production was always below the detection limit in this experiment in agreement with the work of others.

Ni²⁺ Ions Concentration in Water During Reaction

Figure 4 shows a steady rise of Ni²⁺ detected by ICP-MS in water and H₂ production detected by GC as a function of time during the reaction. Material which was suspended in DI water, sonicated for 10 mins and stirred for 20 mins without the light exposure was used as the initial sample. The concentration of Ni²⁺ in this initial sample was below the detection limit. This shows that there was negligible loss of Ni without light indicating that the change is Ni photo-corrosion. The amount Ni ions released into solution was compared with the total amount of H₂ produced. The amount of Ni in solution almost matched the H₂ production.

Structure-Reactivity Relations

To study the mechanism for the deactivation and build a structure-reactivity relationship, another experiment was carried out under similar conditions. Suspensions of materials were taken from the reactor and dropped onto TEM grids after 80 mins, 120 mins and 180 mins of photo-reaction. TEM images were recorded in order to determine the structural evolution during activation/de-activation.

Figure 5a and 5b show two examples of the significant morphological changes that were observed in the core-shell material when close to 50% deactivation. Figure 5a shows that Ni metal has completely vanished from the center of the particle and that a void remains between the TiO₂ and NiO shell. Figure 5b shows a partial void formed at the interface of the Ni metal and TiO₂. In a partial void, some of the Ni metal remains but the contact area between the metal

and the TiO₂ semiconductor is reduced. The percentages of complete void and partial void structures were measured based on over 30 different areas on each sample after 80 min, 120 min and 180 min of the reaction. The results are given in Table 1. The percentage of partial voids increased at the beginning and then decreased with longer exposure in water. The number of complete voids increased with light exposure time and reached 41% of the total areas checked after 180mins. This indicates the partial void structures are early stages of complete void-shell structures. From the TEM images, the void first forms at the interfaces of Ni metal and TiO₂ and then expands to replace the whole metal particle. Charge transfers from the TiO₂ to Ni metal will be impeded by the voids formed at the interface of Ni metal and TiO₂ semiconductors negatively impacting hydrogen production. The loss of contact between the Ni metal and TiO₂ is believed to be one reason for deactivation. Morphology was also checked for materials stirred for 4hrs without light exposure. No significant voiding was observed which proves that the core-shell to void shell conversion is a photo-induced change.

For the materials used in the reactions, 27 μmol of Ni was present on the TiO₂ in the form of both the NiO shell and Ni metal core. Based on the TEM images, the volume ratio of NiO and Ni is close to 1.5:1 and the density of NiO to Ni is about 0.75:1. So the ratio of Ni in NiO and in Ni metal is 1.15. That means there is 13 μmol of Ni metal in the material. According to the TEM observations, 41% of the 13 μmol (5.3 μmol) has been converted to Ni²⁺. According to ICP, the amount of Ni²⁺ in solution after 180 mins reaction is 4 μmol . Thus the TEM and ICP results are in reasonable agreement. .

TEM images were also taken on R500-TO and O500-TO before and after 4hrs Xenon lamp irradiation in liquid water as shown in Figure 6. Figure 6a and 6b show rounded Ni metal

particles on TiO₂ and the morphology is maintained after irradiation. NiO particles look more faceted and are more irregular in shape. The NiO morphology is unchanged before and after irradiation. HRTEM confirmed the particles are still Ni metal and NiO after irradiation for R500-TO and O500-TO respectively. The fact they do not show a structural change is consistent with the absence of photo-reaction activity.

The microscopy, photoreaction and ICP measurements suggest a possible mechanism for the photocorrosion of Ni. Hydroxyl radicals OH· are known as major reactive species in photoreactions.³⁶⁻³⁸ In this case Ni atoms diffusing through the NiO shell, are oxidized by an OH· radical to Ni²⁺ and dissolve in H₂O. A possible reaction pathway for the mechanism is:

This mechanism shows why the concentration of Ni²⁺ and H₂ match over time. It also explains of the absence of O₂ because most of the light induced holes are used to oxidize Ni to Ni²⁺ via the OH· radical reaction. As shown in Scheme 1a, the OH· radicals relevant to the Ni photocorrosion are produced from the holes accumulated in the NiO shell. These OH· radicals are produced in the vicinity of the Ni metal core. The much slower photocorrosion on the pure Ni sample highlights the importance of locally generated radicals. Those results also reflect the fact that Ni/NiO core/shell structures are critical to catalyze the photoreactions. The observation

and reaction mechanism show that H_2 is produced by a photochemical reaction. This reaction is not catalytic with respect to the Ni because it is consumed during the reaction.

The possible mechanisms for the core/shell conversion to void/shell are depicted in Scheme 1b. The examination about the partial void structures, which is the early stage of the structural change, suggests that the voids mostly nucleate at Ni, NiO and TiO_2 triple points. Analysis of the morphological evolution indicates that the core-shell conversion to void-shell structures is more likely on particles having large height/length ratio and high contact angles i.e. particles which are more weakly bonded to the TiO_2 . It is possible that cracks or openings may occur at these weakly bonded interfaces which allow water to directly contact with Ni metal facilitating the Ni oxidation reactions.

However, among the many images recorded, not many cracks are observed. The core-shell to void-shell structure conversion we observed suggests another possible mechanism which relates to a Kirkendall effect similar to that observed during thermal treatment of Ni metal on silica at $400^\circ C$ in oxidative atmosphere.³⁹ Ni metal diffuses several orders of magnitude faster than O along NiO grain boundaries.⁴⁰ That results in a Kirkendall effect where Ni diffuses from the core through the NiO shell onto the surface. The fast Ni diffusion results in vacancies on the Ni metal which then coalesce and form voids. For this photoreaction, based on measurements of the thickness and outer diameter of NiO layers as a function of time, no change of the thickness of the NiO shell was observed. Thus all the Ni reaching the surface is oxidized to Ni^{2+} in agreement with the ICP measurement.

Interestingly, the thermal diffusion rates of Ni and O through NiO are both very low at room temperature under which the photoreactions were performed. This raises the question about the

nature of the photoinduced mechanism for Ni diffusion. One possible explanation is that the light absorbed in the Ni particle results in local heating which can drive the Ni diffusion process.

However a careful calculation indicates that, at the fluxes employed in this experiment, the absorption of light can result in a theoretical local temperature rise of $\sim 10^3$ K/s in an isolated Ni particle. However all this excess heat is rapidly conducted through the thin NiO layer to water resulting in no temperature rising. The exact mechanism for this photo-induced diffusion remains unknown. *In-situ* TEM characterization experiments are ongoing to further explore the photo induced Ni diffusion and oxidation.

One final observation was that the aged material showed a heterogeneous structure with many Ni/NiO core/shells that were completely intact and unchanged after extensive irradiation in water. Since these structures were present in the deactivated form of the material they must not be active for H₂ production. This is consistent with the observation that the Ni in these structures did not undergo photocorrosion. It is interesting to speculate on why these structures did not undergo photocorrosion. It may be that the underlying TiO₂ was highly defective with many e-h recombination centers resulting in very little charge transfer to the co-catalyst. Alternatively, it may be that the interfacial structure of these particles is unfavorable and blocks charge transfer across the heterostructure. Thus the presence or absence of photocorrosion may provide a probe for identifying electrically active interfacial structures that promote charge transfer. Future work in this area may be able to elucidate interfacial characteristics that can facilitate charge transfer across these heterostructures.

Conclusions:

Ni/NiO core/shell on TiO₂ was prepared and tested for photocorrosion in liquid water. H₂ evolution was detected but no O₂ was produced. The H₂ production rate gradually dropped because the core-shell structures transformed to hollow NiO shells. The loss of Ni metal from the

core was the primary reason of deactivation. ICP-MS was utilized to determine Ni^{2+} concentration in the solution before and after reactions. An increase of Ni^{2+} in the water was detected and matched the amount of H_2 produced. Thus the void formation was the result of Ni oxidation and dissolution during light illumination. This photocorrosion occurred either due to direct contact with the water through cracks or a Kirkendall effect where Ni diffused along grain boundaries in the NiO shell onto the particle surface where dissolution took place. Although the core/shell structure of Ni/NiO was effective in decreasing the back reaction and raising the H_2 production rate, it was not able to protect the Ni metal core from photocorrosion. The H_2 evolution was generated by a photochemical reaction which involved photocorrosion of Ni metal. To design a better photocatalyst with this core/shell structure, a kinetic barrier resistant to both O diffusion and the metal diffusion should be considered.

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Figure 1. a) and b) 1 wt% NiO/Ni core/shell on TiO₂ initial material showing core-shell structure. c) Fast Fourier Transform of image b) showing spots matching Ni cubic (111) and (220) and NiO cubic (111) and (200) planes.

Figure 2. a) STEM image of Ni/NiO core/shell structure on TiO_2 ; b) Ti L-edge peaks at the shell position; c) EELS Ni L-edge; d) O K-edge intensity as a function of position along line scan. The left side is the interface with the vacuum and the right side the interface with TiO_2 .

Figure 3. H₂ production rate versus time for three different materials. H₂ production rates are below detection limits for R500-TO and O500-TO NiO.

Figure 4. Plot of amounts of Ni²⁺ in 50ml water and H₂ produced during reaction.

Figure 5. a). Partial void-shell structure areas of deactivated materials show cleavages in between TiO_2 and Ni metal b). Void/shell structures after 50% deactivation

Figure 6. TEM images of R500-TO and O500-TO before and after light irradiation in water: a) initial R500-TO; b) R500-TO after 4 hrs light irradiation in liquid water; c) initial O500-TO; d) O500-TO after 4hrs light irradiation in liquid water. No significant morphological change has occurred.

Time of reaction in liquid water under light	% of partially voids	% of fully voids
Initial	0%	0%
80mins	7%	5%
120mins	2%	11%
180mins	2%	41%

Table 1. Percentage of void/shell areas during deactivation of materials.

Scheme 1. Schematic drawing of the mechanism for Ni/NiO core-shell structure photocorrosion: a) Energy diagram showing Ni as the reduction sites and NiO as the oxidation sites. $OH^\cdot$ radicals generated at NiO shell which is adjacent to Ni metal core oxidizes Ni to Ni^{2+} ; b) illustration of possible progress of the core/shell to void/shell conversion.

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