Importance of characterising the cocatalyst structure in the development of photocatalysts for the splitting of water

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Abstract. In the development of new photocatalysts the surface of materials with some known catalytic activity is modified by the addition of cocatalysts such as partially oxidised nickel. The exact structure of these cocatalyst nanoparticles potentially has a large effect on the properties of the material as they are expected to act as electron traps and increase the catalyst activity. In the partially oxidised nickel system the cocatalyst structure is expected to consist of a metallic nickel core surrounded by a nickel oxide shell, however there is often little characterisation data to support this. In the present TEM study of the supposed NiO/Ni/InTaO₄ system it was found that there was diffusion or migration of the indium possibly from the photocatalyst into the cocatalyst, which is suggested to be a nickel indium oxide surrounding a mixed nickel indium alloy nanoparticle.

1. Introduction

The conversion of solar energy is a desirable option in the development of alternative fuel sources, in particular for the photocatalytic conversion of water into hydrogen and oxygen. An ideal material suitable for this type of reaction has yet to be reported, though several promising developments have been made. An ideal photocatalyst would exhibit certain characteristics, such as long term stability, optimum absorption of the solar spectrum, and the ability to oxidize and reduce water to O₂ and H₂ respectively. Stable oxide semiconductors have shown the best results, with the possibility of manipulating the valence and conduction bands of the materials through alteration of the composition and structure allowing the required redox behaviour. However, the materials previously developed in this field have found limited commercial success for various reasons including a low overall efficiency, as they only utilize the high energy UV periphery of the solar spectrum [1].

Photocatalysts with an appropriate energy band gap split water by absorbing a photon, creating separated electrons and holes in the conduction and valence bands. If the potential difference is greater than that required to split water (1.23 eV) the charges move to the surface and react with water to produce H₂ and O₂. Despite much research on photocatalysis, in particular on materials such as titanates, tantalates and niobates [2], there are at present no materials with a band gap near the theoretical value, and as a consequence methods to try and improve these materials are undertaken. Cocatalysts, such as Pt, RuO₂ and NiO, are intentionally added to the surface of the photocatalyst to act as electron traps and hydrogen evolution sites, so increasing the activity of the catalyst [3].

One examined system has been the addition of partially oxidized nickel to InTaO₄ [3]. The nickel source is added to InTaO₄, then reduced to form metallic Ni, followed by oxidation to form a nickel
oxide shell [3]. It is believed in this case that the Ni-NiO structure is important in the separation of the holes and electrons that are produced after the absorption of a photon in the InTaO$_4$ photocatalyst. The nickel section of the cocatalyst is thought to be useful for the transport of the electrons from the photocatalyst to the NiO surface, where the reduction of water to hydrogen takes place. The presence of the NiO is essential as a metallic nickel surface would actually catalyse the recombination of the produced H$_2$ and O$_2$, the backwards reaction of water splitting [3].

Despite the importance implicated in this cocatalyst structure, and the extensive amount of catalyst testing conducted upon this system, there is often little direct evidence of the suggested NiO/Ni/InTaO$_4$ structure. Consequently we have investigated this system with electron microscopy techniques, attempting to determine the cocatalyst structure.

2. Experimental

The Ni-modified InTaO$_4$ photocatalyst was prepared via a literature method [3], specifically a 1 wt% cocatalyst was achieved through the addition of Ni(NO$_3$)$_2$, and the material calcined in air for 1 hour at 350 °C, reduced in H$_2$ for 2 hours at 500 °C and oxidized in O$_2$ for 1 hour at 200 °C.

TEM analysis was conducted on an FEI CM200 FEG TEM running at 197 kV equipped with an Oxford Instruments Energy Dispersive X-ray (EDX) spectrometer and a Gatan Imaging Filter. Samples were prepared by dispersing in methanol, with a drop placed on a holey carbon coated copper grid. SEM samples were coated with a thin layer of platinum and examined in a LEO 1530 Gemini FEG SEM with Oxford instruments EDX spectrometer. Powder X-ray Ray Diffraction (XRD) was performed on a Bruker D8 powder diffractometer. Photocatalyst testing was performed (0.1 g of catalyst, 110 mL H$_2$O) with a Xe lamp (300 W) and the evolved gases were analyzed by gas chromatography-mass spectrometer for 20 hours.

3. Results and Discussion

The partially oxidized nickel doped InTaO$_4$ system was characterized four times during the synthesis and testing process; the initial unmodified InTaO$_4$, the reduced system Ni/InTaO$_4$, the oxidized system NiO/Ni/InTaO$_4$, and then this latter material after photocatalytic testing. Powder X-ray diffraction patterns of the nickel modified materials only showed reflections attributable to the photocatalyst InTaO$_4$. SEM analysis was performed to measure the size of both the photocatalyst and added cocatalyst, with an average InTaO$_4$ particle diameter measured at 256 nm, and the smaller cocatalyst particles generally being in the range of 15 to 40 nm in diameter.

Initial TEM examination of the nickel added materials show the smaller cocatalyst nanoparticles on the larger photocatalyst particles (figure 1). The material after oxidation appears to have a core-shell structure (figure 1(b)) as opposed to the particles after only reduction (figure 1(a)).

Figure 1. TEM images of 1 wt% Ni added to InTaO$_4$ (a) after reduction (b) after oxidation (c) after photocatalyst testing

The material retains this core-shell structure even after photocatalytic testing, as viewed in figure 1 (c). The cocatalyst particles in the material after testing are not significantly different from those in...
the oxidized sample in either size or crystallinity, indicating that they are stable under the reaction conditions. This is of particular importance, as it has previously been found that during photocatalytic testing the material can be deactivated due to nickel being eluted and redeposited [4].

The requirement to confirm the presence of particular elements within the materials led to studies by EDX spectroscopy. Initial analysis confirmed the presence of oxygen, nickel, indium and tantalum, but in an attempt to more precisely determine the elemental distribution through the material, dark field STEM and EDX maps were recorded (figure 2). In the EDX maps produced from the material after oxidation, it is possible to see the locations of Ni, In and Ta. The nickel signal (figure 2 (b)) is concentrated in areas corresponding to the small cocatalyst particles, while the tantalum signal (figure 2 (d)) corresponds closely to that of the photocatalyst particles, the same particle shape being seen in the Ta EDX map and the STEM image. However something different is seen in the indium EDX map (figure 2 (c)), here is a similar coverage to that shown in the tantalum EDX map, but there also appears to be several locations where there are concentrated areas, which correspond with the nickel signal and the small cocatalyst particles.

![Figure 2](image.png)

**Figure 2.** The material after oxidation (a) DF STEM image, with arrow showing location of linescan (b) Ni K EDX map (c) In L EDX map (d) Ta M EDX map (e) linescan of Ni, In and Ta across a nanoparticle into the photocatalyst

This suggestion of indium being present in the cocatalyst particles as well as nickel was confirmed by an EDX linescan across one of the cocatalyst particles, as indicated by the arrow in figure 2 (a). The EDX linescan (figure 2 (e)) shows both nickel and indium, in similar concentrations across the cocatalyst particle. The tantalum signal is only apparent once the electron beam is in the photocatalyst particle, at which point the nickel signal drops off and the indium signal mimics that of the tantalum, but at a lower level. This indicates that the cocatalyst unexpectedly contains both nickel and indium, while the photocatalyst contains only indium and tantalum; this is also found to be the case in the reduced material. There are known nickel indium alloys, such as Ni$_3$In, Ni$_2$In, NiIn and Ni$_2$In$_3$, which can form at temperatures similar to those used in the preparation of these materials [5], and studies on thin films of nickel and indium have shown diffusion at quite low temperatures [6]. The exact source of this indium is unconfirmed; it may come from unreacted In$_2$O$_3$ from the InTaO$_4$ synthesis, however as this mixed Ni-In system is found in all examined cocatalyst particles it is more likely that the source of indium may be the neighbouring photocatalyst particle. This migration or diffusion of atoms from a material to a supported catalyst has been discussed before, in terms of strong metal-support interaction [7], for instance in which titania has been observed to migrate over supported Pt.

TEM images of the oxidized materials (both before and after testing) indicated a core-shell structure, initially believed to be NiO/Ni, and with this new evidence of indium in the cocatalyst,
differences between the two layers were investigated. The presence of oxygen was confirmed with an EFTEM map (figure 3 (b)), showing oxygen to be mainly present in the photocatalyst and edge of the cocatalyst. The spinel structure, NiIn$_2$O$_4$, has previously been reported [8] however its preparation from In$_2$O$_3$ and NiO was performed under harsh conditions and the reaction did not go to completion. The lattice fringes that are present in the shell of the oxidized material have been measured (figure 3 (c)) and do not correspond to NiO or to any of the reported nickel-indium alloys. No crystallographic details are available for nickel indium oxides, although data is available for CuIn$_2$O$_4$ and Cu$_2$In$_2$O$_5$ which may have similar structures, and these do have lattice spacings similar to those measured in this system.

![Figure 3](image)

**Figure 3.** Nominal NiO/Ni/InTaO$_4$ system: (a) TEM image (b) EFTEM oxygen map showing oxide shell on cocatalyst (c) area of TEM image showing lattice fringes in the oxide shell

4. Conclusions
Considerable importance is placed on the cocatalyst structure in photocatalytic systems. In this study we have examined what was believed to be a NiO/Ni/InTaO$_4$ system. Despite the material being synthesised in conditions similar to those previously examined in the literature, it was determined that indium, possibly from the photocatalyst migrated or diffused into the added cocatalyst, forming an inner mixed nickel-indium alloy surrounded by a nickel indium oxide. The exact composition and structure of the cocatalyst has not been determined at this point, but hopefully with further experiments comprising electron energy loss spectroscopy and electron diffraction this should be accomplished. Diffusion of indium from the underlying photocatalyst may have important effects in terms of the magnitude of the band gap and hence photon absorption.

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