

Designing Semiconductor Photocatalyst/ Metal Cocatalyst Composites for Water Splitting

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One potential method for the conversion of solar into storable energy is the use of semiconductors (so called photocatalysts) which mediate the decomposition of water to hydrogen and oxygen. Oxide semiconductors are a common choice due to their corrosion resistance and the possibility of engineering their band gaps via doping. However application of these materials is currently limited because of a low overall efficiency, due to absorption being confined to the UV periphery of the solar spectrum, rapid electron-hole recombination, and potentially poor surface chemistry. To overcome the latter two problems 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, thus increasing activity. In this paper we detail a structural investigation of the semiconductors NiTa₂O₆ and InTaO₄ decorated with nickel/nickel oxide core shell cocatalyst nanoparticles, similar to those presented in the literature [1, 2] and draw some general conclusions about the design of such co-catalysts.

Cocatalysts were synthesized by adding a soluble nickel salt to the photocatalyst, which is then reduced to form metallic Ni nanoparticles dispersed on the photocatalyst surface, followed by oxidation to form a nickel oxide shell. It is assumed that the NiO/Ni core shell structure is important for the separation of the electrons from the holes which are produced after the absorption of a photon in the photocatalyst. The nickel interior of the cocatalyst is thought to mediate electron transfer to the NiO surface and prevent back electron transfer due to a Schottky barrier. At the NiO surface the reduction of H⁺_(aq) to hydrogen gas occurs. The presence of the NiO is essential as a metallic nickel surface would rapidly catalyse the recombination of H₂ and O₂ to water and prevent acidic dissolution of Ni metal.

Analytical TEM/STEM and aberration corrected dedicated STEM [3] has revealed the following features of these materials:

- (a) It has provided the first real evidence for the existence of the cocatalyst (metal) core-(oxide) shell structure (Fig. 1);
- (b) It has provided evidence for degradation of the nickel cocatalyst during photocatalysis of the NiO/Ni:NiTa₂O₆ material (Fig. 2). In the case of nickel it appears to form nickel hydroxide;
- (c) It has provided evidence for interdiffusion between the photocatalyst and the cocatalyst in the case of the nominal NiO/Ni:InTaO₄ material (Fig. 3). The interdiffusion involves diffusion of In from the InTaO₄ photocatalyst into the Ni co-catalyst to form a crystalline Ni₃In alloy with an oxidised shell, which also contained indium, considered to be Ni_{1.25}In_{0.75}O₃ based on EELS and XPS data. Furthermore, there also appears to be variation between particles of different size. It is important to note that the nickel-indium cocatalyst nanoparticles formed were very stable, appearing to maintain their structure even after catalytic testing, which contrasts with the partially oxidised nickel:NiTa₂O₆ system that exhibits structures attributable to dissolution/redeposition of nickel. However catalytic activity appeared to be reduced.

In this study we have examined two semiconductor photocatalyst systems, each coated with a nickel containing cocatalyst, and despite being processed using analogous conditions to those described in the literature, the resulting cocatalyst structures are complex and photocatalyst dependent which may be the reason for the apparent variation in results between different groups.

References

- [1] H. Kato, A. Kudo, *Chem. Phys. Lett.* **1998**, 295, 487 - 492.
 [2] Z. Zou, J. Ye, K. Sayama, H. Arakawa, *Nature* **2001**, 414, 625 - 627.
 [3] N. S. Hondow, et al. , *J. Phys.: Conf. Series*, Vol. 241 doi: 10.1088/1742-6596/241/1/012036

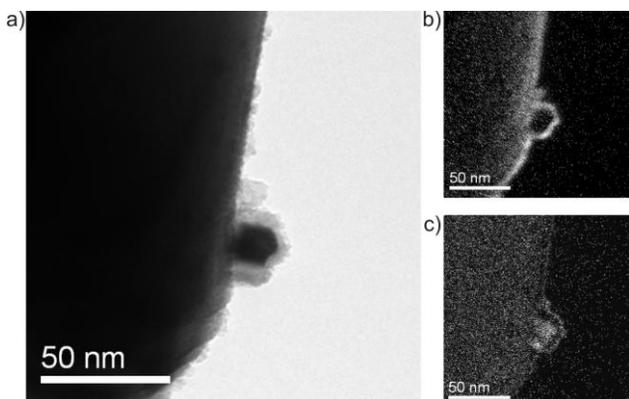


Fig. 1. Nominal 1 w/w% NiO/Ni:NiTa₂O₆ a) TEM image of a core shell nanoparticle on a NiTa₂O₆ particle; b) EFTEM oxygen *K* element map; c) EFTEM nickel *L* element map.

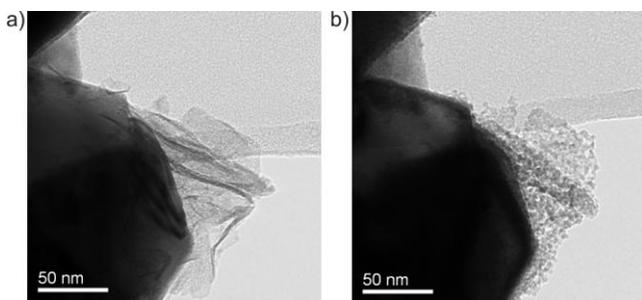


Fig. 2. Before and after EELS analysis of nominal 1 w/w% NiO/Ni:NiTa₂O₆ a) Ni containing area that no longer looks like a core shell nanoparticle, suggesting Ni(OH)₂ formation; b) The same area after being examined in the TEM for *ca.* 3 min.

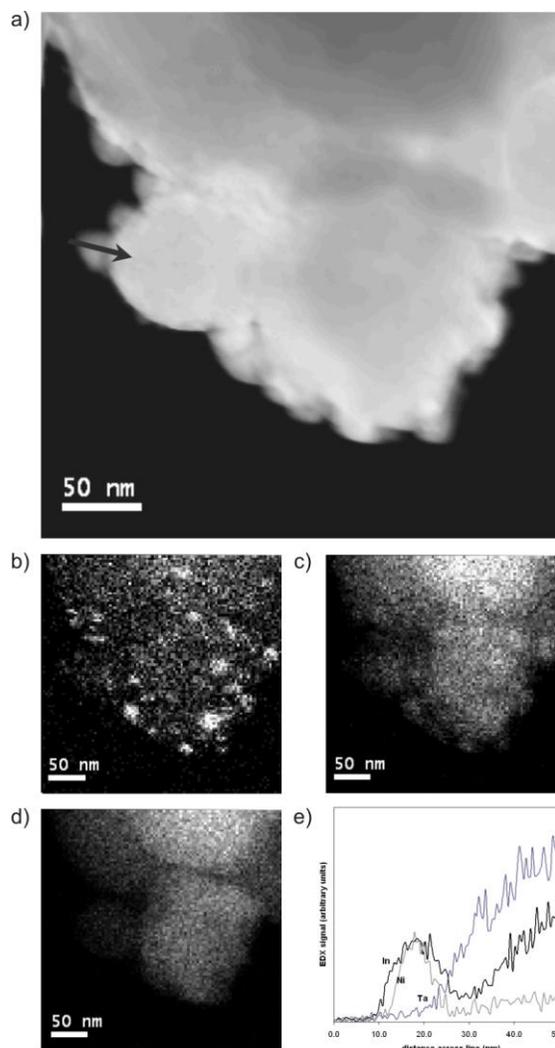


Fig. 3. The nominal NiO/Ni:InTaO₄ material after oxidation a) DF STEM image, with arrow showing location of linescan; b) Ni *K* EDX map; c) In *L* EDX map; d) Ta *M* EDX map; e) EDX linescan of Ni *K*, In *L* and Ta *M* across a nanoparticle into the photocatalyst.