

Abstract

The scientific community is researching alternative renewable and clean energy sources to shift from fossil fuels. The conversion of solar energy into useful chemical energy such as hydrogen production via photocatalysis is a promising process to contribute to these alternatives, with much effort being focused on the development of photocatalysts for photocatalysis. The deposition of noble metal nanocluster co-catalysts can modify the properties and improve the efficiency of photocatalysts. The use of noble metal nanoclusters consisting of a few atoms as co-catalysts has attracted considerable attention due to their unique electronic and catalytic properties. However, it is challenging to maintain the cluster co-catalysts' size due to the clusters' tendency to agglomerate to form larger particles and lose their cluster-like properties. Another challenge that co-catalysts face is the back reactions of water splitting such as water formation from hydrogen and oxygen on the co-catalysts.

An overlayer of thin metal oxide on a co-catalyst-modified photocatalyst plays a critical role in photocatalysis reactions by stabilising the co-catalysts and suppressing the back reactions. This thesis makes an original contribution to our knowledge on the chromium oxide layer formed onto photocatalysts and gold cluster-modified photocatalysts by performing physical, chemical, electronic and catalytic studies on this layer.

The stability of the CrO_x layer photodeposited onto different crystal phases of TiO_2 films and P25, $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ and $\text{Al}:\text{SrTiO}_3$ particles with subsequent annealing at temperatures up to $600\text{ }^\circ\text{C}$ was investigated (Please note that the layer is labelled " CrO_x " until the nature of the Cr component is confirmed (*vide infra*)). After annealing, for TiO_2 films, CrO_x layer diffuses into the amorphous and anatase phases of TiO_2 film but remains stable at the surface of the rutile phase. Moreover, for particles, CrO_x mostly diffuses into P25, while for $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$, the degree of CrO_x diffusion is less than that into P25. Interestingly, the CrO_x layer is very stable on the surface of $\text{Al}:\text{SrTiO}_3$ particles. This diffusion is attributed to the strong metal–support interaction effect between CrO_x and different photocatalysts. Moreover, some of the CrO_x was reduced to metallic Cr after annealing but there was no observation of the high oxidation state of Cr. The particles' bulk and surface band gap structures were also investigated, along with the photocatalytic water splitting activity.

For the first time, chemically synthesised phosphine-protected gold clusters, $\text{Au}_9(\text{PPh}_3)_8(\text{NO}_3)_3$, deposited onto RF-sputter deposited TiO_2 film are prevented from agglomeration after the removal of ligands. This effect is achieved by photodepositing the CrO_x layer on the top of the clusters as a protective layer. Further, the influence of heat treatment on the surface roughness of two different thicknesses of RF-sputter deposited TiO_2 films and the effect this has on size-specific Au_9 clusters

deposited on the surface was also investigated. It is found that the high mobility of the thick TiO_2 film after heating leads to a significant agglomeration of the Au_9 clusters, even when protected by the CrO_x layer. However, the thin TiO_2 film has much lower mobility when heated, resulting in non-agglomerated clusters with CrO_x coverage.

In the last part of this thesis, the stability of Au_9 clusters beneath a $\text{Cr}(\text{OH})_3$ layer onto SrTiO_3 particles under conditions of photocatalytic water splitting (i.e., UV irradiation) was investigated. After a photocatalytic water splitting reaction for seven hours, Au_9 clusters without the CrO_x layer were found to agglomerate into large particles, while the application of the CrO_x layer resulted in the inhibition of the agglomeration of Au_9 clusters.