Investigation of Ligand Protected Gold Clusters on Defect Rich ALD Titania using Electron Spectroscopies

Abstract

The use of sunlight for the photocatalytic conversion of carbon dioxide into useful chemical fuels has gained attention in recent years. The high photocatalytic activity can be achieved with help of the efficient heterogeneous photo catalyst in which the catalyst possesses a different state of matter (gas, liquid and solid) compared to the reactant or products. Gold nanoclusters in few nanometre dimensions exhibit distinct electronic properties with the change in the size of the clusters. These discrete properties make them unique for photocatalytic applications. Titania is a widely used metal oxide support for heterogeneous catalysis. The pre-treatment of the substrate plays a critical role in the photocatalytic reactions and helps in the strong attachment of the nanoclusters with the substrate which results in high catalytic activity.

In this research, atomically precise chemically synthesised ligand protected gold cluster were used as the metal nanoclusters. The chemically synthesised gold nanoclusters are protected by the triphenylphosphine ligands and therefore the size of the cluster is controlled. The atomic layer deposition (ALD) titania was employed as the metal oxide support as it has a flat uniform surface making it suitable for surface studies. The pre-treatment of the ALD titania was performed by heating to remove hydrocarbons and sputtering to create oxygen vacancies prior to the deposition of the gold nanoclusters onto the surface of the ALD titania. The deposition of the chemically synthesised clusters onto the surface of the titania was performed by the solution-based deposition method. The triphenylphosphine ligands were removed by heat treatment in ultra-high vacuum at 200°C for 20 minutes thus creating contact of the gold nanoclusters with the substrate. The interaction of the gold nanoclusters with the titania substrate can be studied with a combination of the surface analytical techniques such as Metastable Induced Electron Spectroscopy (MIES), X-ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS) and Inverse Photoemission Spectroscopy (IPES). In this research, ALD titania was used as the metal oxide substrate which has the flat uniform surface makes it beneficial for the surface studies. Metastable Induced Electron

Spectroscopy (MIES) is an extreme surface sensitive analytical technique used to study the outermost valence electronic structure of the sample surface. X-ray Photoelectron Spectroscopy (XPS) is used to study the chemical composition of the sample surface. The Ultraviolet Photoelectron Spectroscopy (UPS) and Inverse photoemission spectroscopy (IPES) are used to study the valence and conduction band electronic structure. Thus, the combination of the Ultraviolet Photoelectron Spectroscopy (UPS) and Inverse Photoemission Spectroscopy (IPES) gives the complete band structure of the sample surface.