

# Abstract

Solar hydrogen as a renewable source of energy has been the focus of research for the past decade. Enhancement of the properties of photo active metal oxide anodes for better bias-free production of solar hydrogen through photoelectrochemical water splitting continues to be a thrust area in the quest for sustainable energy solutions. Among foremost materials, challenges for this application such as highly efficient photo catalysts, cost factor and long term stability are the main factors for material selection. Earth abundant metal oxides such as  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  are promising candidates in terms of their stability and cost. However, their poor electrical properties are major limiting factor for using them as possible photoanodes. Last decades, multiple improvement techniques have been employed for overcoming these challenges such as carbon/MOx material, doping, surface functionalization, multi-layer systems and nano-structuring of the metal oxides.

The major research objective of this thesis was to establish plasma-assisted chemical vapor deposition techniques for growing high-quality graphene on various substrates due to its excellent electrical properties. Availability of fabrication procedures enabling direct growth of graphene would allow convenient handling (no need of post-synthesis transfer) and enable the combination of graphene with other functional material. Low-pressure plasma-chemical decomposition of hydrocarbons (primarily methane) was fully investigated as viable approach. Graphene growth in conjunction with transition metal oxide films ( $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ ) was investigated to design bi- and multilayer electrodes for better light harvesting and superior charge transport. In addition to thorough material characterization graphene-based nanocomposite electrodes were tested as photoanode material for photoelectrochemical splitting of water.

In this work, enhancement of charge carrier separation, light absorption, and stability of graphene/hematite nanocomposite photoanodes for solar hydrogen production were studied. Graphene was deposited using Plasma-enhanced CVD with methane as the carbon source in a hydrogen-free process with substrate temperatures as low as 250 °C.

As-grown graphene sheets on copper foil were also used as a seed layer for epitaxial assembly of reduced graphene oxide (r-GO) flakes from solution at room temperature. The reactivity of graphene with the metal ions during the PECVD process was limited by preventing charge accumulation at the graphene surface. Single and multilayer graphene films were characterized using atomic force microscopy, scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and Raman spectroscopy. Additionally photocurrent densities of the new electrodes were measured to understand their charge carrier densities and transport behavior.

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> films electrodes were deposited in a plasma-enhanced chemical vapor deposition setup using Fe(CO)<sub>5</sub> and Ti(O<sup>i</sup>Pr)<sub>4</sub> as molecular precursors. Multilayered electrodes ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/graphene/TiO<sub>2</sub>) were built through the utilization of few layer graphene (FLG) sheets and self-aligned rGO (SAG) films in combination with TiO<sub>2</sub> that showed superior photocurrent densities and onset potentials over pristine metal oxide electrodes ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>) and even the bilayer electrode ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>). This enhancement is attributed to better charge carrier separation at the metal oxide and graphene interface. Moreover, TiO<sub>2</sub> functionalization (bilayer) of the hematite electrode showed significant enhancement in the long term stability of as deposited hematite electrodes through passivation of hematite's surface trap states.

Hematite layers deposited (PECVD) at higher temperatures showed a more dense structure. Subsequently leading to an enhancement in light absorption and charge carrier density due to increased photo induced electron/hole pair separation. Hematite electrodes deposited at higher temperatures displayed higher photocurrent densities over pristine hematite, 3.8 and 1.6 mA.cm<sup>-2</sup> at 1.8 V vs RHE respectively. Moreover, hematite electrodes deposited at higher temperature showed increased hydrogen production, observed in the long-term chronoamperometry measurements of the electrodes.

Hematite electrodes co-doped (In and Sn) through multi-layering displayed enhanced optical properties, explaining the superior photocurrent density and onset potential of the co-doped electrodes (4.33 mA.cm<sup>-2</sup> at 1.8 V vs RHE with 0.75 V onset) over the pristine hematite electrodes. Furthermore, the ITO under-layer shows direct effect on

the amount of carbon impurities, left over by the precursor decomposition (carbonyl group) during the deposition process, attributed to the diffusion of oxygen (from the ITO under-layer) during the annealing process to the deposited thin film, thus leading to the oxidation of the carbon impurities.