CHAPTER 1

INTRODUCTION

Photovoltaic devices are based on the concept of charge separation at an interface of two materials with different conduction mechanism. Normally between solid - state materials, both n - and p - type regions with electron and hole majority carriers in a single semiconductor material, hetero - junctions between different semiconductors or semiconductor - metal (Schottky) junctions. In photo - electrochemical cells, the junctions are semiconductor - electrolyte interfaces. Electrochemical photovoltaic cells have the following advantages when compared with Si based photovoltaics. First, they are insensitive to defects in the semiconductor materials. Second, the solid/liquid junction is easy to form and thus is economical to manufacture. Third, it is possible to realize direct energy transfer from photons to chemical energy in electrochemical photovoltaic cells. An electrochemical photovoltaic cell is generally composed of a photoactive semiconductor working electrode and a metallic counter electrode (e.g. Pt). Both electrodes are immersed in electrolyte containing suitable redox couples. If the semiconductor–electrolyte interface is illuminated with light having energy greater than the bandgap of the semiconductor, photogenerated electrons/holes are separated. The photogenerated minority carriers arrive at the interface of the semiconductor–electrolyte, while the majority carriers accumulate on the back face of the semiconductor. With the help of a charge-collecting substrate, photogenerated majority carriers are transported via a load to the counter electrode where these carriers electrochemically react with the redox electrolyte [1, 2].

The dye-sensitized solar cell (DSSC) is the newest photovoltaic device configuration. First developed by O’Reagan and Grätzel in 1991, this class of cell has reached efficiencies of over 11% [3]. The basic structure of a DSSC involves a transparent (wide-band-gap) n-type semiconductor configured optimally in a nanoscale network of columns, touching nanoparticles, or coral-like protrusions. The surface area of the network is designed to be huge, and it is covered everywhere with a monolayer of a dye or a coating of quantum dots, which functions as the dye. The dye sensitizer is the absorber. An electrolyte is then used to permeate the resulting coated network structure to set up a conduit between the dye and the anode. The dye absorbs light, producing excitons, which dissociate at the dye-semiconductor interface, resulting in photogenerated electrons for the semiconductor and oxidized dye molecules that must be reduced - and thereby regenerated - by the electrolyte. The transparent semiconductor network provides the path to the cathode for the photogenerated electrons. The liquid electrolyte is the pathway from the anode for the reducing species which provide electrons for the oxidized (hole-bearing) dye molecules. The diagram of Figure 1.1 shows the constant production of the electrolyte reduced species at the counter electrode and the constant supplying of electrons via the semiconductor to the external circuit to do work. The semiconductor forming the network coated with dye molecules or quantum dots needs to be transparent to allow light to reach the absorber materials, and the network must have a huge surface area to provide the dye amount required for absorption. The electrolyte must be able to permeate the whole network to give electrical continuity; consequently, liquid electrolytes have proven very effective [4].

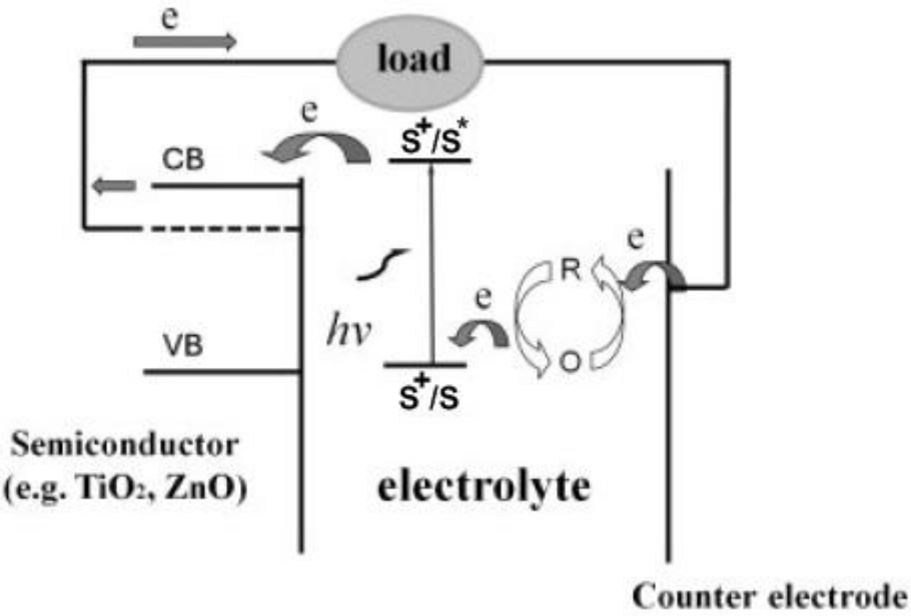

Figure 1.1 Operating mechanism of a Wet-type DSSC. S: dye sensitizer, S*: excited dye sensitizer, S^+: oxidized dye sensitizer, O/R: redox couple (e.g. I_3^-/I^-) [2].

A ruthenium dye was initially employed in the DSSC, but by now several organic dyes and inorganic quantum dot "dyes" have been explored. Initially, TiO_2 (anatase) was used as the transparent, n-type semiconductor network, but other TCO-type semiconductors have been utilized, including SnO_2 and ZnO. Alternatives to the liquid electrolyte have included gels and solid-phase hole conductors [4].

Important drawbacks of the dye-sensitized solar cell are the volatility of the electrolyte and the corrosive action of the iodide redox couple. Correspondingly, long-term application of dye-sensitized solar cell is limited by the electrolyte permeability of the encapsulation and its inertness towards the iodine. A lot of effort has therefore invested in finding less volatile electrolytes while maintaining sufficient hole transport. Approaches to replace the liquid electrolyte include application of ionic conducting polymer gels, electrolyte gelled with amino-acid derivatives or room temperature molten salts. Complete replacement of the liquid electrolyte system has been established using inorganic p-type semiconductors, such as CuI or CuSCN as well as organic hole conductors, including low molecular weight charge transport materials and semiconducting polymers [5].

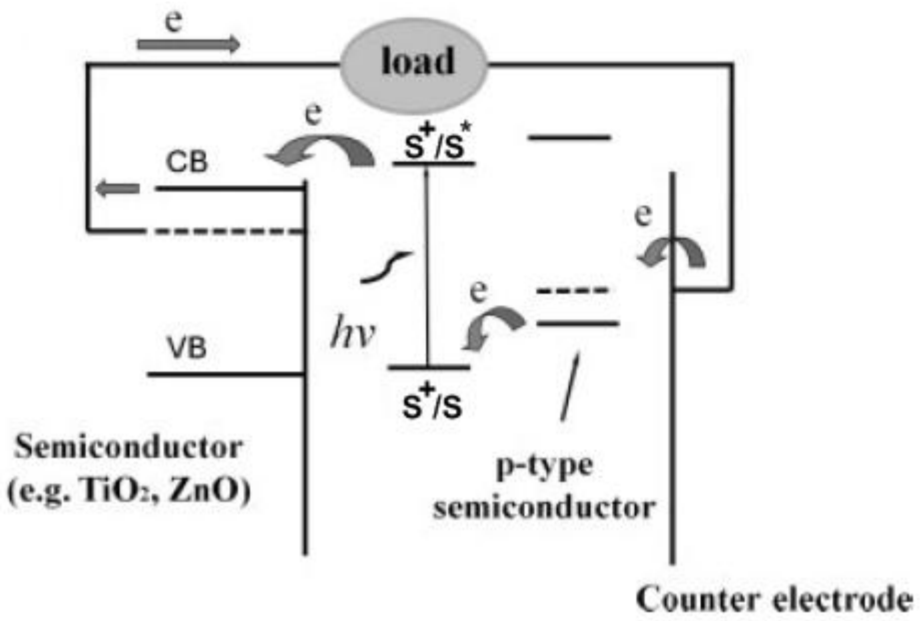

Figure 1.2 Operating mechanism of an electrochemical solid-state DSSC with a p-type semiconductor replacing the electrolyte containing the redox couple [2].

In a DSSC, the initial photoexcitation occurs in the light absorbing dye as shown in Figure1.2 Nanoporous semiconductors such as TiO_2 not only act as support for the dye sensitizer but also function as electron acceptor and electronic conductor. Subsequent injection of electrons from the photo-excited dye into the conduction band of semiconductors results in the flow of current travelling across the nanocrystalline TiO_2 film to the charge collecting electrode and then to the external circuit. Sustained conversion of light energy is facilitated by regeneration of the reduced dye sensitizer either via a reversible redox couple (O/R), which is usually I_3^- / I^- (Figure 1.1) or via electron donation from a p-type semiconductor (Figure 1.2) [2].

The most common approach to fabricate solid-state DSSCs is by using p-type semiconductors. Several aspects are essential for any p-type semiconductor in a DSSC [6,7]:

(1) It must be able to transfer holes from the sensitizing dye after the dye has injected electrons into the n-type semiconductor (TiO_2, ZnO, SnO_2 etc.); that is, the upper edge of the valence band of p-type semiconductors must be located above the ground state level of the dye.

(2) It must be able to be deposited within the porous nanocrystalline layer.

(3) A method must be available for depositing the p-type semiconductors without dissolving or degrading the monolayer of dye on n-type semiconductor nanocrystallites.

(4) Ionic species must be incorporated into the three dimensional n-type semiconductor layers to enhance the electron diffusion in the nano-porous n-type semiconductor phase.

(5) It must be transparent in the visible spectrum, or, if it absorbs light, it must be as efficient in electron injection as the dye.

This research concentrate on synthesize p – type semiconductors (Copper sulfide (CuS) and Aluminium antimonide (AlSb)) which can be used as hole conductor in composite electrolyte DSSCs.

Copper sulfides are the IB-VIA compounds having different phases, such as covellite (CuS), anilite (Cu_7S_4), digenite ($Cu_{1.8}S$), djurleite ($Cu_{31}S_{16}$) and chalcocite (Cu_2S). CuS is one of semiconducting materials, which have a wide variety of applications: optical filters and cathode materials in lithium rechargeable batteries and p – type semiconductor of solar cells [8, 9]. There are different methods used to produce this compound: solvothermal-microwave process [10], and solvothermal reactions [11]. On the other hand of them is AlSb, which has wide variety applications photovoltaic cells, p-n junction diodes, and anodes for Li-ion batteries. It is zinc-blende structure with a lattice constant of 0.6126 nm, and high melting point (1,058 ^{o}C). Generally, AlSb is the p-type intrinsic semiconductor. By doping with Se, Te and S as donors, it transforms into the n-type extrinsic one. In this research, both of CuS and AlSb nanocrystals were produced by the direct flow of electrons through solid mixtures, and further characterized. This process is novel, fast, effective, and friendly to the environment.

Research objectives

1. Design, build and assemble the vacuum system use for control pressure as copper sulfide and aluminium antimonide synthesis by using solid-state direct current heating.
2. To synthesize and characterize copper sulfide and aluminium antimonide powder with nanometer and micrometer structures by the direct flow of electricity through solids.
3. To fabricate quasi-solid-state dye-sensitized solar cells base on copper sulfide composite electrolyte and characterize their electrical properties.