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Hydrogen Energy and Photoelectrolysis of Water

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ABSTRACT

Hydrogen is an environmentally friendly energy source that can replace fossil fuels. An efficient low cost photoelectrolysis system would be an ideal way to store solar energy as hydrogen. Among semiconductor materials those can be used in photoelectrolysis, cuprous oxide is an attractive material. Preliminary investigation of electrodeposited cuprous oxide films demonstrates the possibility of photoelectrolysis of water for hydrogen production.

Introduction

Level of consumption of energy is a major factor that determines the standard of living. Indeed, energy is central to many economic and environmental issues. The global consumption of energy is rapidly increasing and finding the supply to this demand is a difficult and challenging task. Adequate and reliable supplies of affordable energy, obtained in environmentally sustainable ways, are essential to economic prosperity, environmental quality, and political stability around the world (1). Major environmental concerns such as acid rains and green house gas emissions, with their potential for global warming and climate impacts, arise principally as a consequence of energy production. Energy supply and energy efficient technologies represent the major share in the global market today.

As at present, fossil fuels provide about 85 % of the world's energy. With the demand of energy, fossil fuels will continue to provide world's energy for at least for a few more decades. However, in addition to the depletion of fossil fuel reserves, concerning the global climate change due to carbon dioxide emission, acid rains, etc., there is a strong need to search for low carbon or non carbon fuels. To meet the long-term emission levels targeted, it would require more than order of magnitude increase in energy from non-carbon-emitting sources.

Hydrogen as an energy source

A variety of alternative fuels has been suggested that could address the environmental and energy supply problems. Among them hydrogen offers the greatest potential in the environmental and energy - supply benefits. Indeed, hydrogen is considered as *the fuel of the 21 st century* and already the *hydrogen economy* has been set in progress. Hydrogen is an energy carrier like electricity and it can be produced from hydrocarbons and electrolysis of water(2-4).

Hydrogen can be burnt to release energy in internal combustion engines and there the emission is only water. With direct injection, hydrogen engines can be run at higher compression ratios than gasoline engines, increasing engine efficiency. Hydrogen engines are 20-25% higher in efficiency than comparable gasoline engines and practical hydrogen engines can achieve efficiencies of about 45%. Efficiencies could be further increased with fuel cells, where electricity is produced directly using hydrogen and oxygen. Figure 1 shows a schematic diagram of a fuel cell. Hydrogen at the anode dissociates into protons and electrons. The anode is separated from the cathode by an electrolyte that can conduct protons but not electrons. To reach the cathode, electrons must travel through the external circuit producing an electric current. The protons and electrons combine at the cathode to produce water and waste heat. The theoretical electrical conversion efficiency for an ideal hydrogen-oxygen fuel cell is 85% and in practical cells it is around 60%. Fuel cells are relatively expensive and current research effort focuses onto the reduction of this cost. Long term research initiatives are in progress on developing hydrogen and fuel cell transportation technologies.

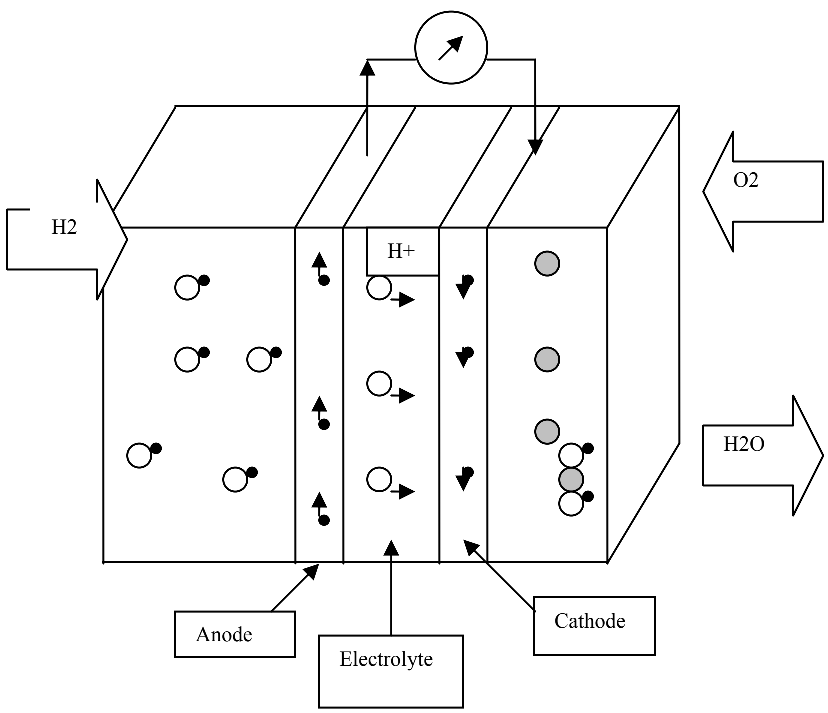

Figure 1: Schematic diagram of a fuel cell

Further, hydrogen will provide an ideal storage medium for renewable energy. Production of hydrogen from renewable sources such as wind, solar would allow the energy to store, transport and generate electricity when and where it is needed, as they are intermittent.

Production of Hydrogen

Hydrogen production systems are already available and widely used in the chemical and oil refinery industries. More than 90% of hydrogen is produced today thermochemically, where hydrocarbons are reacted with steam or oxygen to produce hydrogen. When low cost electricity is available, water electrolysis is also used to produce hydrogen. Here, electricity is passed through a conducting aqueous electrolyte, breaking down water into hydrogen and oxygen.

Photoelectrolysis

Fundamental research is being carried out to use sunlight directly to produce hydrogen in a photolectrochemical cell. The possibility of producing H_2 using UV light in a phtoelectrocehemical cell was first demonstrated by Fujishima and Honda in 1972 using the semiconductor material titanium dioxide (TiO_2) [5]. Since then, a large number of semiconductor materials have been investigated for photoelectrocatalytic electrodes for H_2 production.

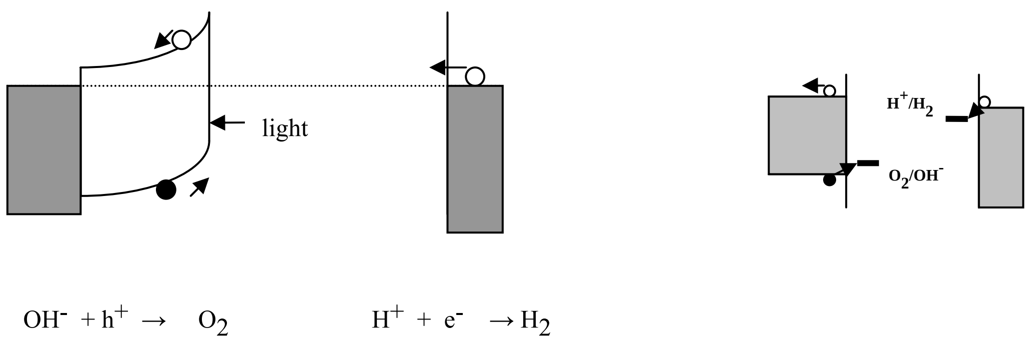

Figure 2: Schematic representation of the photoelectrolysis process

As shown in the fig. 2, in such devices sunlight produce electron-hole pairs in the semiconductor in contact with an aqueous electrolyte. The electrons combine with protons and produce hydrogen at the counter electrode while the holes oxidize water to oxygen at the semiconductor electrode. Although many semiconductor materials have shown photocatalytic activity, most of them suffer from limitations including photocorrosion, poor solar spectrum absorption and the need of external bias [6]. Indeed, TiO_2 is one of the most studied oxide semiconductor materials in this regard because of its stability in aqueous electrolytes. However, the band gap of TiO_2 (3.2 eV) limits the absorption of sunlight to the high-energy portion (UV) of the solar spectrum. It has been reported earlier that attempts have been made to improve the absorption of visible light of TiO_2 by incorporation of substitutional atoms into the lattice. Although the incorporation of transition metals improves the visible light absorption in TiO_2 electrodes, they have not yet been shown to have proper band gap and band positioning to be suitable for efficient water splitting reactions.

The technique of photoelectrolysis is still far from commercialization due to the high cost, low efficiency and low stability of the semiconductor electrodes. To be able to commercialize a photoelectrolysis system it needs at least a10% conversion efficiency. Recently 12% efficiency has been reported for a photoelectrolysis system (7).

Phtoelectrolysis of water with cuprous oxide

The search for the efficient photoelectrolysis of water to produce hydrogen is continuing. The real challenge is to find a suitable low cost semiconductor material, stable in aqueous electrolyte with a proper band positioning.

Wide band gap semiconductor materials (2.5-3.5 eV) are typically more stable compared to narrow band gap (0.8-2 eV) materials; however, the solar spectrum is more efficiently absorbed by the narrow band gap materials. Thermodynamically, the energy requirement for the water splitting reaction is 1.23 eV. However, considering the loss mechanisms such as series resistance and the electro catalytic over potential, the optically-produced electron hole pairs need an energy difference of approximately 2 eV for efficient photoelectrolysis [8]. Cuprous oxide is a semiconductor having a direct band gap of 2 eV which has been studied previously for application in solar energy converting devices (c.f. [9] and references therein). A major attraction of cuprous oxide is that it is inexpensive, non-toxic, and readily available. Cuprous oxide can be prepared using many techniques including electrodeposition. The major disadvantages of cuprous oxide are that it is unstable with respect to anodic photocorrosion and it has a relatively low electrical conductivity [9].

The advantages of the chemical stability of TiO_2 and the photon absorbance spectrum of Cu_2O with their conveniently aligned interface band structure to form n-TiO_2/p-Cu_2O heterostructure will be an interesting system for the possible application in photlectrolysis of water (10). Specific problems and questions that have to be addressed in this system include, (a) Is there a simple, reliable, and potentially low-cost fabrication procedure for heterojunction formation? (b) What are the photoelectrochemical properties of the junction? (c) Will the device perform stably over a range of pH values? (d) What can be done to optimize the performance?

Electrodeposition of Cu_2O films on metal substrates can be accomplished in a three-electrode electrochemical cell containing aqueous solutions of 0.05 M sodium acetate and 0.05 M cupric acetate [11]. The heterojunction can be formed by electron beam evaporation of TiO_2 (100 nm) over the electrodeposited Cu_2O. Photoelectrolysis process of the Cu_2O/TiO_2 electrodes has been evaluated in an electrochemical cell containing a 0.1 M sodium acetate solution with a platinum counter electrode (10).

The photocurrent is a measure of the generation of hydrogen. The photocurrent measured as a function of bias voltage under chopped illumination from the Cu_2O/TiO_2 photocathode is shown in fig.1. It is evident from the figure that for an efficient hydrogen production an external bias is required for this system.

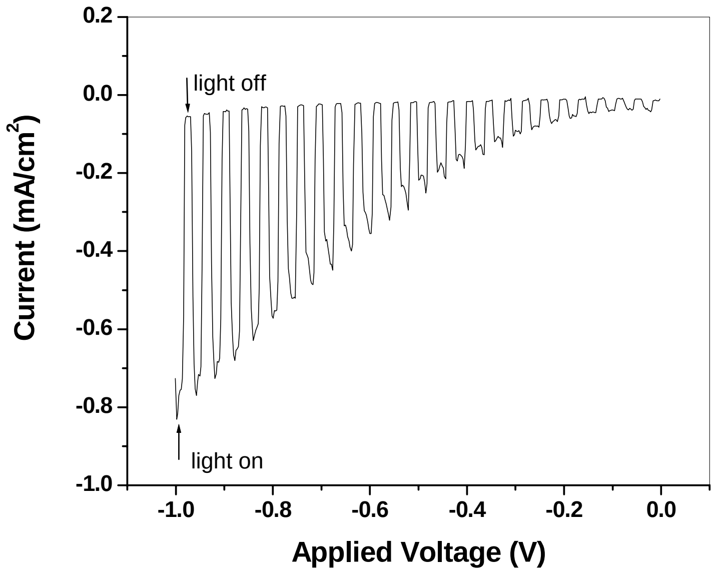

Figure 3: Chopped light current –voltage characteristics of the Cu2O/TiO2 electrode

As it is evident in figure 3, although Cu2O is a direct gap material the long wavelength is weaker. If this contribution is increased substantial increase in the efficiency in the phoelectrolysis process could be expected.

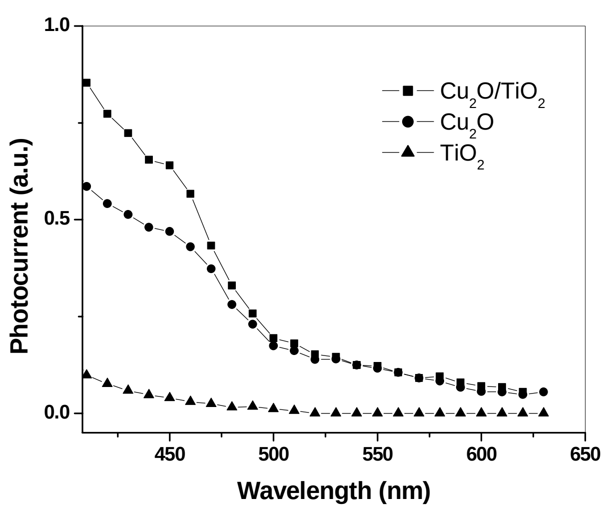

Figure 4: Spectral response of Cu2O/TiO2 electrode

The absolute efficiency for H_2 generation of the heterostructure is equivalent to $1.6x10^{-6}$ mMH_2/W. Assuming an energy equivalent of $2.8x10^5$ Joules/mole for H_2 the energy conversion efficiency (including the required bias, 1 V @ 390 μA) was 0.5%.

The stability of the Cu2O/TiO2 is demonstrated with the fig. 5. At various acidic and basic conditions of the electrolyte, the electrode produced reasonable photocurrent without detereating the electrode. This is an encouraging result and it demonstrates the possibility of developing this system using composite semiconductor materials.

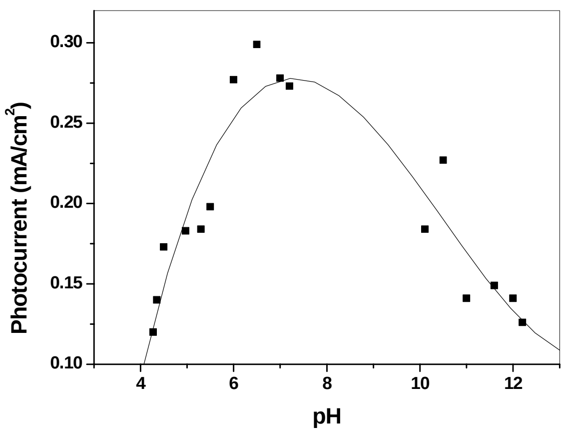

Figure 5: Photocurrent variation of the Cu2O/TiO2 electrode in electrolytes with different pH values.

Other possibility of using the Cu2O electrodes in photoelectrolysis process would be the preparation of the films in n-type form. Result of a preliminary investigation has shown the ability to produce hydrogen without applying an external bias.

Conclusions

Hydrogen is a clean source of energy that can be used in combustion engines or directly convert to electricity using fuel cells. It can be considered as a storage medium for solar energy. An efficient low cost photoelectrolysis process would be a suitable mechanism for producing hydrogen at large scale. Preliminary investigation of electrodeposited cuprous oxide demonstrates the possibility of photoeltrolysis of water for hydrogen production but the efficiency is very low.

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