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# Efficiency of solar water splitting using semiconductor electrodes

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**Abstract**

Reliable measurement of the photoconversion efficiency for semiconductor electrodes is essential to the assessment of electrode performance. In this paper, the influence of the choice of light source on measured photoconversion efficiencies for semiconductor photoelectrodes is examined. Measurements of efficiency performed under xenon lamp and solar illumination are compared with efficiencies calculated by integrating the incident photon conversion efficiency (IPCE) over the lamp and solar spectra. It is shown that use of a xenon lamp as the light source can lead to a large overestimate of the photoconversion efficiency, relative to that obtained under standard AM1.5 solar illumination. The overestimate is greater when a water filter is fitted to the xenon lamp, and when a wide-band gap semiconductor such as $TiO_2$ is used as the photoelectrode. Achievable photoconversion efficiencies using rutile $TiO_2$ are calculated taking into account the losses due to imperfefct absorption, reflection and charge-carrier recombination; these calculated efficiencies agree with the measurements to within experimental uncertainties. It is demonstrated that many photoconversion efficiencies presented in the literature are overestimated. It is concluded that reliable estimation of efficiency under standard conditions is best obtained by measuring the IPCE as a function of wavelength, and integrating over the AM1.5 solar spectrum, or by measuring under sunlight with a similar zenith angle to that of the AM1.5 spectrum.

*Keywords:* Hydrogen generation; Solar energy; Photoelectrochemistry; Photoelectrolysis; Photocatalysis; Spectral irradiance; Xenon lamp; Solar spectrum; Semiconducting materials; Titanium dioxide

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## 1. Introduction

Photoelectrochemical splitting of water to produce gaseous hydrogen using solar energy has been researched intensively since its initial demonstration in 1972 [1]. The most important figure of merit for a semiconductor photoelectrode is the photoconversion efficiency for water splitting, which is defined as the ratio of the chemical potential energy stored in the form of hydrogen molecules to the incident radiative energy. The benchmark efficiency is 10%, which is generally considered to be required for commercial implementation [2].

Most measurements of the photoconversion efficiency are performed under illumination by artificial light sources. This is convenient for many reasons—the artificial sources are stationary, and their intensity is essentially constant with time, while the spectrum and intensity of solar radiation reaching the ground depends on the time of day, atmospheric conditions such as cloud cover, water vapour content and ozone column,

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albedo of the surrounding ground, etc. However, the comparison of photoconversion efficiencies obtained for different semiconductor materials requires that these efficiencies are presented for a standard solar spectrum, usually the AM1.5 global solar spectrum, and artificial light sources do not accurately replicate such spectra.

An examination of the literature reveals that in most cases the photoconversion efficiency values presented are obtained using illumination by a particular artificial light source. For example, Nozik [3] used a UV source with radiation between 300 and 400 nm to measure photoconversion efficiencies of up to 4% for $TiO_2$ photoelectrodes. Giordano et al. [4] obtained an efficiency of 2.7% for a $TiO_2$ electrode doped with platinum using a mercury lamp. Khan and Akikusa [5] quoted an efficiency for flame oxidised titanium of 2.0%; the publication indicates a xenon lamp was used, but Akikusa's PhD thesis [6] reveals that a mercury–xenon lamp was used. Akikusa and Khan [7] reported an efficiency of 1.6% for a similar photoelectrode under xenon lamp illumination. Khan et al. [8] claimed an efficiency of 8.35% for a flame-pyrolysed titanium photoelectrode with a band-gap extended to 535 nm by carbon doping; again xenon lamp illumination was used. Mishra et al. [9] obtained photoconversion efficiencies as high as 3% for $TiO_2$ photolectrodes using a mercury–xenon lamp source. Tang et al. [10] reported an efficiency of 2.5% for a mesoporous anatase photoelectrode using a xenon lamp. Radecka et al. [11] obtained an efficiency of 1.9% using a xenon lamp for a mixed anatase and rutile thin film deposited by radio-frequency sputtering.

As will be shown later, all of these efficiency figures are close to or higher than those that are thermodynamically possible for the standard AM1.5 global solar spectrum, given the band gap of the semiconductor material used and the bias voltage applied. It therefore seems likely that the efficiencies are larger than those that would be obtained for sunlight.

In this study, we investigate the influence of the light spectrum on the photoconversion efficiency for cells with semiconductor photoelectrodes. We consider in particular the most widely used source, the xenon arc lamp. We have had the spectrum of our lamp characterised by an accredited standards laboratory. We examine the influence on efficiency of the spectrum of the lamp, both with and without a water filter fitted. Water filters are widely used to absorb the infrared output of the lamp, thereby decreasing the heating of the irradiated surfaces. We also investigate the influence of the age of the lamp tube on the spectrum.

The photoconversion efficiency depends on many factors in addition to the spectrum of the incident radiation. These include the band gap of the semiconductor, reflection of radiation before reaching the semiconductor, the level of absorption of the radiation in the semiconductor, and the transport of charge carriers through the semiconductor. We examine the influence of each of these factors on the achievable efficiency, both for solar illumination and xenon lamp illumination.

We have measured the photoconversion efficiency for a cell with a rutile $TiO_2$ photoelectrode under both xenon lamp and solar illumination. We have also measured the incident photon conversion efficiency (IPCE), which is the efficiency of conversion of photons incident on the photoelectrochemical cell to photocurrent flowing between the working and counter electrodes, as a function of wavelength of the incident radiation. This allows the photoconversion efficiency to be calculated for any radiation spectrum. The efficiencies obtained from the measurements are compared with those calculated taking into account the spectrum of the radiation, the band-gap, the absorption and reflection of the radiation, and transport of the charge carriers.

The measurements reported here were obtained at room temperature ($T = 295\,\mathrm{K}$). The effect of increased temperatures on water splitting efficiencies has been investigated by Licht [12,13].

In Section 2, we present the details of our measurements, including the characterisation of the light sources, and the results of these measurements. Our calculations of the efficiency limits for the different light sources are given in Section 3. The measurements are compared with the calculations in Section 4; in addition, the results of other workers are discussed in the light of our results, and possible means of increasing the photoconversion efficiency of semiconductor electrodes are considered. Conclusions are presented in Section 5.

## 2. Experimental details and results

### 2.1. *Sample preparation*

The specimen used in this study was prepared by oxidising a titanium substrate in a methane and oxygen flame. Before oxidation, the titanium sheet (Sigma Aldrich, 99.7%, 0.25 mm thick) was polished and then etched in Kroll's solution (one part 40% HF, one part 70% $HNO_3$ and three parts water) for 5 s. A small (6 mm × 6 mm) piece of the sheet was held in a methane–oxygen flame for five minutes, at a position at which the flame temperature was measured to be 850 °C using a K-type thermocouple. The oxygen to methane volume ratio of the gas mixture was 1.15, so