

Tuning of suitable solar spectrum onto photocatalytic materials of the matched band gap using optical engineering

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In this report, we have carried out work on the concept of optical engineering for tuning solar spectrum onto photocatalytic materials of the matched band gap using a holographic concentrator. Processing parameters of holographic concentrators have been designed suitably to have a control over the desired wavelength range for photocatalytic materials of the matched band gap.

Keywords: photocatalytic materials, holographic concentrator, diffraction efficiency, solar spectrum.

1. Introduction

Depletion of fossil resources and other environmental issues have become a matter of serious concern, and researchers are now expected more strongly than ever to contribute to the realization of sustainable development. It has been estimated that the amount of available solar energy on the surface of the Earth is much higher than the total energy consumption by mankind. Therefore, the development of an efficient solar energy conversion system could be of tremendous help in meeting our future energy requirements. Solar energy conversion has been carried out by various means: solar thermal, photovoltaics, solar water splitting, *etc.* Storage is the ultimate problem associated with all the means, beside one (solar water splitting). The conversion of solar energy into chemical fuel (hydrogen gas) by water splitting is becoming more and more attractive due to the above specific feature related to the storage of energy. At the same time, the development of a clean and renewable energy carrier that does not utilize fossil fuels is

a great technological challenge. However, industrial H₂ production consumes huge amounts of fossil fuels (*e.g.*, natural gas), resulting in equally large CO₂ emissions. Photocatalytic water splitting using semiconductor electrodes has thus attracted considerable interest due to its potential for clean production of H₂ from easily available water by utilizing abundant solar energy in nature [1–9]. The field is highly interdisciplinary, involving principles of physical chemistry (electrochemistry, photochemistry, interfacial charge transfer and surface science), semiconductor physics (electronic band structure, solid-state charge transport and materials science) and optical engineering (dispersive and concentrating system). Ever since FUJISHIMA and HONDA [10] reported photoelectrochemical water splitting using a TiO₂ electrode in 1972, numerous researchers have reported more than 100 photocatalytic materials based on metal oxides. The major problems associated with photocatalytic materials are the inefficiency in sunlight due to large band gaps as well as the instability in aqueous solutions. Several materials have shown promising efficiency but suffer from poor stability; whereas, other materials are favored due to their high corrosion resistance but they suffer from large band gaps. Maximum solar absorption can be attained by minimizing the semiconductor band gap. However, if the band gap becomes too small, the cell will not generate enough potential to drive the water splitting reaction. In order to split water in a PEC cell, the conduction band-edge potential of a semiconductor electrode must be lower than that of the hydrogen-evolving half reaction and its valence band-edge potential must be higher than that of the oxygen-evolving half reaction [11]. Hence the band gap engineering to cover up the entire solar spectrum and at the same time dispersing and concentrating system for solar spectrum onto photocatalytic materials of the matched band gap jointly play an important role in enhancing the solar water splitting technology. In this report, we have carried out the work on the concept of optical engineering for tuning solar spectrum onto photocatalytic materials of the matched band gap using a holographic concentrator [12]. To validate the theoretical prediction, a comparison of theoretical and experimental variation of diffraction efficiency with wavelength for a typical holographic concentrator recorded on a high resolution silver halide plate has been presented. Here designed parameters have been optimized to have maximum efficiency operation for on-Bragg angle illumination. However, with the change in angular position of the sun, *i.e.* with the change in the angle of illumination, diffraction efficiency falls [13]. Thus tracking mechanism becomes mandatory to have maximum efficiency operation throughout the day. The optical system that has the smallest *f*-number allowed by the sine inequality, which has been called an ideal light collector, would have an *f*-number equal to 0.5, a physically unrealizable limit [14]. Concentration ratios are related to *f*-number of the system. Although *f*-number 1 is most suitable for photovoltaic concentrator applications [15, 16], yet for the purpose of experimental investigation, the holographic concentrator of *f*-number 4.5 has been recorded and its diffraction efficiency has been determined. Nowadays dichromated gelatin [17], photopolymers [18], PQ/PMMA [19] are being used extensively for recording holographic optical elements, however due to the ease of availability and cost effectiveness of source and recording materials, we have re-

corded holographic concentrators on a commercially available high resolution silver halide plate PFG-01 [20]. Such concentrators may be a viable alternative to conventional concentrators used for photo-enhancement in PEC system [21–23].

2. Photocatalysis

A typical photocurrent-generating device having a semiconductor in contact with an electrolyte, is often referred to as photoelectrochemical cells. It consists of a photoactive semiconductor working electrode (either *n*- or *p*-type), an electrolyte containing a redox system, and an inert counter electrode made of either metal or semiconductors. There are hundreds of semiconductor electrodes being reported till date (some of them are listed in Table 1) but most of them function only under ultraviolet region, due to large band gap energy of the materials. Such an energy range is present in less than 5%, whereas nearly half of the solar energy incident on the Earth’s surface lies in the visible region (shown in Fig. 1).

Table 1. Semiconductor electrodes with different band gap.

Semiconductor	Band gap [eV]	Suitable wavelength [nm]
SnO ₂	3.8	327
TiO ₂	3.2	388
ZnO	3.2	388
SiC	3	414
WO ₃	2.6	477
CdS	2.42	513
GaP	2.25	552
Fe ₂ O ₃	2.1	591
GaInP	1.85	671
CdSe	1.7	730

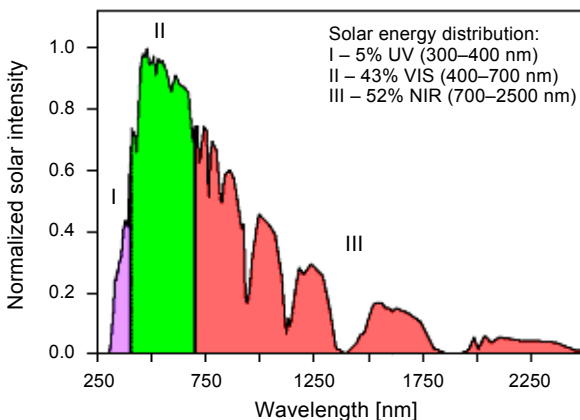


Fig. 1. Solar energy distribution chart.

Table 2. Properties of photoelectrochemical cells. (Reprinted with permission from Ref. [36]. Copyright 1996 American Chemical Society.)

No.	Cell	Band gap [eV]	Suitable wavelength [nm]	Solvent	Photovoltage [V]	Photocurrent [mA/cm ²]	Efficiency [%]
1	<i>n</i> -Cd(Se ₃ Te) / (S ²⁻ S _n ²⁻)	1.7	730	H ₂ O	0.78	22	12.7
2	<i>n</i> -GaAs / (Se ²⁻ /Se _n ²⁻)	1.4	887	NaOH	0.65	20	12
3	<i>p</i> -InP / (V ³⁺ /V ²⁺)	1.3	955	HCl	0.65	25	11.5
4	<i>n</i> -WSe ₂ (Γ/I ₃ ⁻)	1.2	1034	H ₂ O	0.63	28	>14
5	<i>n</i> -MoS ₂ (Γ/I ₃ ⁻)	1.1	1128	H ₂ O	0.55	9	-
6	<i>n</i> -Si(Br/Br ₂)	1.1	1128	H ₂ O	0.68	22	14.9
7	<i>n</i> -Si(Fe/Fe ⁺)	1.1	1128	CH ₃ OH	0.67	20	16
8	<i>n</i> -CuInSe ₂ (Γ/I ₃)	1.0	1241	H ₂ O	0.64	21	9.7

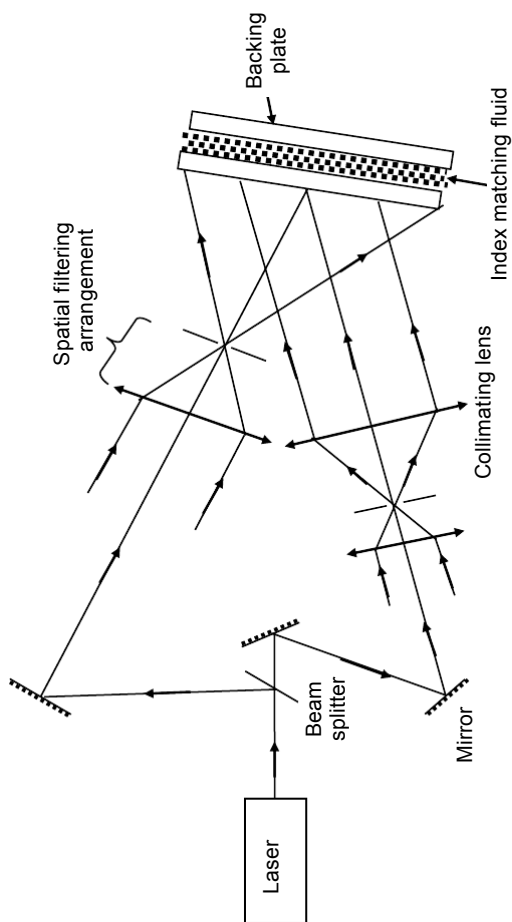


Fig. 2. Schematic of a holographic concentrator recording setup.

A semiconductor material to photoelectrochemically split water must satisfy the following conditions [24, 25]:

- The band gap must be a minimum of 1.7 eV to provide the potential necessary for electrolysis and overcome other energy losses in the system.
- The minority band edge and the Fermi level of the material must straddle the hydrogen and oxygen redox potentials for current to flow through the circuit.
- The material must be stable in contact with the electrolyte.
- Have high efficiency in the conversion of photons to separated electron/hole pairs.
- Additionally, charge transfer at the interface must be fast enough to prevent accumulation of minority carriers at the semiconductor surface that can shift the band edges out of the overlap position.

Based on stability and remarkable conversion efficiencies of available semiconductor electrodes [26–36], some of them are listed in Table 2 along with suitable wavelength.

Different photocatalytic materials are sensitive to different regions of the solar spectrum. Such photocatalytic materials do not make full use of the incident solar energy. The part of radiation not used by the photocatalytic materials causes deterioration in the performance characteristics, particularly as a result of overheating and degradation of the material. Hence in present work we have carried out the work based on the concept of optical engineering for tuning solar spectrum onto photocatalytic materials (listed in Tables 1 and 2) of the matched band gap using a holographic concentrator.

3. Holographic concentrator

Holographic concentrators are recorded using two coherent waves derived from the same laser source. Out of two coherent waves one is a spherical wave and the other is a plane wave. Figure 2 shows a typical geometry for recording the holographic concentrator [13]. Study has been done on optimization of designing parameters of holographic concentrators to have control over the desired wavelength range required for photocatalytic materials with an available band gap.

3.1. Theory

The formula for diffraction efficiency η of a thick phase transmission holographic concentrator, which is illuminated at Bragg's angle, is given by the coupled wave theory [37] assuming refractive index variation to be sinusoidal as:

$$\eta = \sin^2(\nu) \quad (1)$$

where

$$\nu = \frac{\pi n_1 d}{\lambda \cos(\theta)} = \frac{\pi n_1 d}{\lambda \sqrt{1 - \sin^2(\theta)}} \quad (2)$$

where n_1 is the depth of refractive index modulation, d is the film thickness, λ is the free space wavelength of the reconstruction light beam and θ is Bragg's angle.

Bragg's angle θ is related to the fringe spacing Λ recorded in the hologram and average refractive index of the medium (n) through the relation given by

$$\sin(\theta) = \frac{\lambda}{2n\Lambda} \quad (3)$$

Thus for illumination at Bragg's angle the reconstruction diffraction efficiency η can be given as

$$\eta = \sin^2 \left\{ \frac{\pi n_1 d}{\lambda \sqrt{1 - \left(\frac{\lambda}{2n\Lambda} \right)^2}} \right\} \quad (4)$$

Using Eq. (4), the variation in diffraction efficiency η with wavelength at Bragg's angle for different values of film thickness and depth of refractive index modulations of a holographic concentrator has been plotted. While drawing the curves, much care has been taken to ensure that the criteria for thick phase transmission holograms are fulfilled for which Eq. (4) holds good. A holographic concentrator is said to be thick if its Q parameter ($Q = 2\pi\lambda d/n\Lambda^2$) is greater or equal to 10 [38].

3.2. Recording and reconstruction (illumination) of a holographic concentrator

For present work, a holographic concentrator has been recorded on a high resolution silver halide plate PFG-01 (film thickness $d = 8 \mu\text{m}$ and average refractive index $n = 1.61$) using a He-Ne laser ($\lambda = 0.6328 \mu\text{m}$) of power 2 mW. The angle between the plane wave and the reference wave at the time of recording was $\theta = 45^\circ$. Fringe spacing in the recorded hologram was $\Lambda = \lambda/[2n\sin(\theta/2)] = 0.51 \mu\text{m}$. The exposed film was processed using the standard procedure [39, 40].

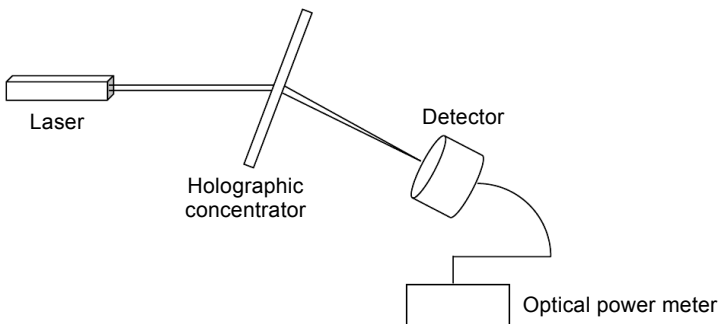


Fig. 3. Schematic of diffraction efficiency measurement setup at Bragg's angle using a laser source.

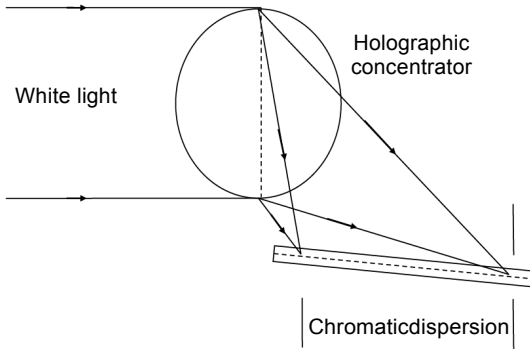


Fig. 4. Schematic of reconstruction setup of a holographic concentrator in white light.

In order to show spectral responses of the recorded holographic concentrator, it was illuminated with available four different wavelength sources (λ) equal to 0.488, 0.5145, 0.532 and 0.6328 μm at optimum Bragg’s position and the output power was measured by an optical power meter (shown in Fig. 3). The recorded concentrator was also played back by a white light source (shown in Fig. 4) to realize the dispersive capacity of the system.

4. Results and discussions

4.1. Simulation results

Processing parameters (e.g., film thickness d and depth of refractive index modulation n_1) of holographic concentrators were optimized suitably for tuning solar spectrum

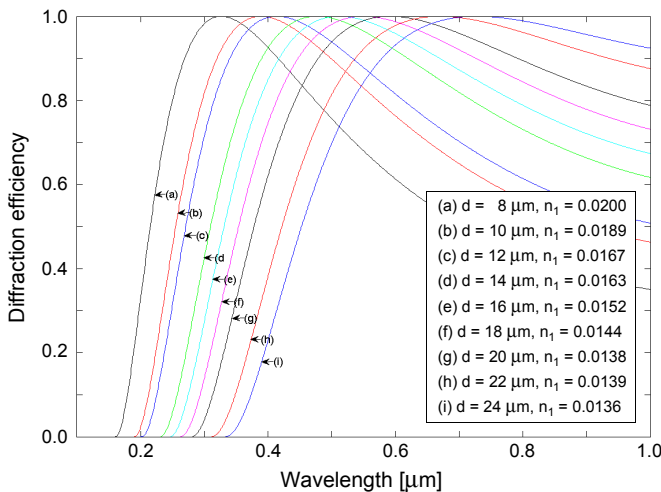


Fig. 5. Variation in diffraction efficiency with wavelength for different values of film thickness and depth of refractive index modulation at fixed value of $\Lambda = 0.51 \mu\text{m}$ and $n = 1.61$.

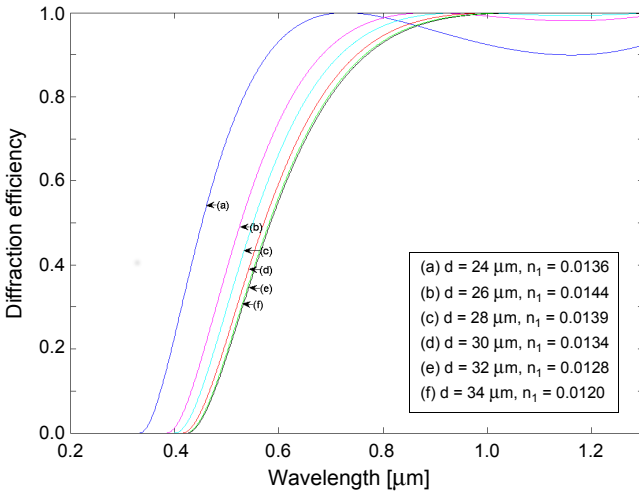


Fig. 6. Variation in diffraction efficiency with wavelength for different values of film thickness and depth of refractive index modulation at fixed value of $\Lambda = 0.51 \mu\text{m}$ and $n = 1.61$.

over the desired wavelength range. For semiconductor electrodes enlisted in Tables 1 and 2, the diffraction efficiency *versus* the wavelength curves were plotted as shown in Figs. 5 and 6, respectively.

4.2. Experimental results

Figure 7 shows experimental verification for the theoretical (simulation) predictions for a typical holographic concentrator. Experimental curve is in a good agreement with the simulated one (curve *a*, Fig. 5) with a slight decrease in diffraction efficiency with

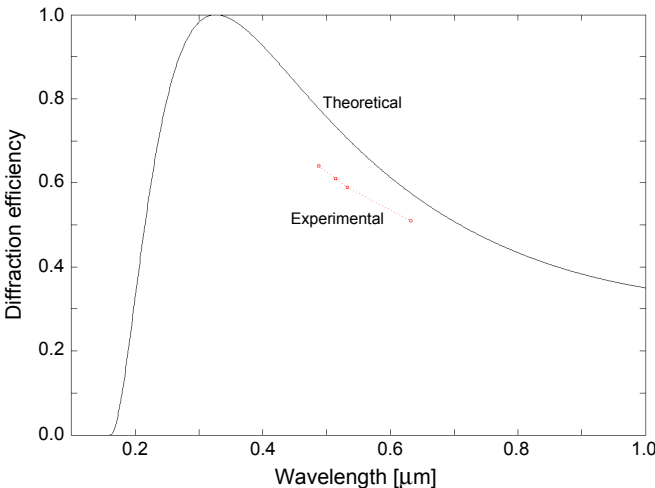


Fig. 7. Variation in diffraction efficiency with wavelength for a typically recorded holographic concentrator ($n_1 = 0.0200$, $\Lambda = 0.51 \mu\text{m}$, $n = 1.61$ and $d = 8 \mu\text{m}$).

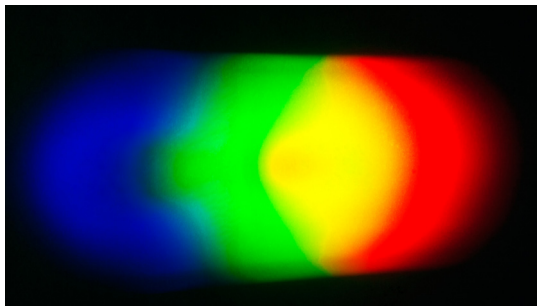


Fig. 8. Photograph of the spectrum of white light diffracted by a typical holographic concentrator.

respect to the theoretical value. The slight decrease in the experimental value of diffraction efficiency with respect to the theoretical value may be due to absorption by the film and loss due to scattering. In order to realize all other simulation curves shown in Figs. 5 and 6, one has to achieve the particular depth of refractive index modulations for corresponding film thickness as specified in the simulation at the time of recording of holographic concentrators.

Figure 8 shows a photograph of the spectrum of white light diffracted by a typical holographic concentrator. Photograph of Fig. 8 reveals that a properly recorded holographic concentrator can efficiently split up white light into its constituent colours.

5. Conclusions

Based on the simulation as well as experimental results, it is concluded that processing parameters of a holographic concentrator can be optimized suitably to achieve appreciable diffraction efficiency over the desired wavelength range necessary for photocatalytic materials with available band gaps. Hence it is quite possible to disperse and concentrate specific wavelengths on photocatalytic materials for their maximum efficiency operation depending upon their band gap. Unwanted portion of solar spectrum which degrades the material and its performance may be filtered out. This may further decrease the cost of photocatalytic material by replacing costly material area with relatively small concentrator area. Further, by properly optimizing processing parameters of holographic concentrators, their chromatic characteristics can be controlled. Thus the holographic concentrator may advantageously be used in photoelectrochemical devices to enhance the efficiency of the system.

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