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Radiative heat transfer and catalyst performance in a large-scale continuous flow photoreactor for hydrogen production

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HIGHLIGHTS

- We designed and analyzed a photocatalytic water-splitting system for continuous operation at a large pilot-plant scale.
- The optimization of photon transfer and mass transfer processes is accomplished.
- Energy and exergy analyses and related parametric studies are performed.
- Radiation from the reactor surface due to reflection and scattering has the largest contribution to exergy losses.
- The energy and exergy efficiencies of the system increase more than 1.5 times by doubling the catalyst concentration.

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ABSTRACT

In this paper, a photocatalytic water-splitting system is designed and analyzed for continuous operation at a large pilot-plant scale. Performance of the photocatalyst and reaction system is discussed, as well as photon transfer and mass transfer limitations (in the case of liquid phase reactions). The optimization of these two processes is a main objective of this study. The system uses an external power source and two electrodes immersed in the catalyst solution to supply and transfer electrons inside two reactors to replace the need for electron acceptors and donors. A nano-filtration membrane, which is utilized to separate hydrogen and oxygen in the reactor, retains the catalyst on the cathode side while allowing passage of other species to the other half cell. A Compound Parabolic Concentrator (CPC) is presented for the sunlight-driven hydrogen production system. Energy and exergy analyses and related parametric studies are performed, and the effect of various parameters are analyzed, including catalyst concentration, flow velocity, light intensity, catalyst absorptivity, and ambient temperature.

1. Introduction

Many efforts have been directed in recent years to the development and characterization of new types of photocatalysts for water splitting and hydrogen production, to absorb visible light (Maeda and Domen, 2007; Chen and Mao, 2007). A mixture of H_2 and O_2 can be obtained from photocatalysts in powder form, while pure H_2 gas is needed as a fuel supply on a large scale. Thus, there is a need to develop better and more efficient devices, based on the use of photocatalysts in the form of thin layers with different arrays, in order to efficiently separate H_2 and O_2 in water photo splitting processes (Kitano et al., 2007).

Selli et al. (2007) have proposed a photocatalytic water-splitting process employing a new two-compartment Plexiglas cell, which allows the decomposition of H_2O separately into H_2 and O_2 on opposite sides of an illuminated photoactive Ti electrode. In the absence of any sacrificial reagent, the photon efficiency of hydrogen production under irradiation with a UV lamp at a wavelength above 300 nm is 2.1%; under irradiation with a VIS lamp ($\lambda > 350$ nm), it decreases to 0.36% (Selli et al., 2007).

A photoelectrochemical device with a molecular Ru catalyst assembled via pH-modified Nafion on a dye-sensitized nanostructured TiO_2 film as the anode and a Pt foil as the cathode has been successfully demonstrated to split water into O_2 and H_2 using visible light as the input. Since the conduction band of TiO_2 is not sufficiently negative to reduce protons to hydrogen directly, a small bias of -0.325 V vs. Ag/AgCl is needed to achieve complete water splitting. Nafion membranes are non-reinforced films based on chemically stabilized perfluorosulfonic acid copolymer in the acid (H^+) form. The strong acidity of commercial Nafion has caused an increase of the overpotential for water oxidation, which led to the fast decay of photocurrent (Li et al., 2010).

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Although there are several reports of visible-light driven photocatalysts developed recently, these compounds can only produce H_2 or O_2 with a relatively low yield owing to the bandgap limitation. To overcome this shortcoming, a novel photocatalytic system called a Z-scheme, which simulates the Z-scheme mechanism in natural photosynthesis of green plants, has been developed (Sayama et al., 1997) to generate H_2 and O_2 simultaneously. The Z-scheme is a dual-photocatalyst system that consists of an H_2-photocatalyst and O_2-photocatalyst to perform water reduction and oxidation, respectively (Bae et al., 2009).

In the Z-scheme, two photocatalysts are mixed in a single reactor to perform photocatalytic water splitting, so that H_2 and O_2 are produced as a mixture. To overcome the problem of combined production, a twin reactor was designed to have $Pt/SrTiO_3$:Rh (H_2-photocatalyst) and WO_3 (O_2-photocatalyst) discretely in two compartments of a connected reactor separated by a modified Nafion ion-exchange membrane to perform the water-splitting reaction under visible-light irradiation (Lo et al., 2010).

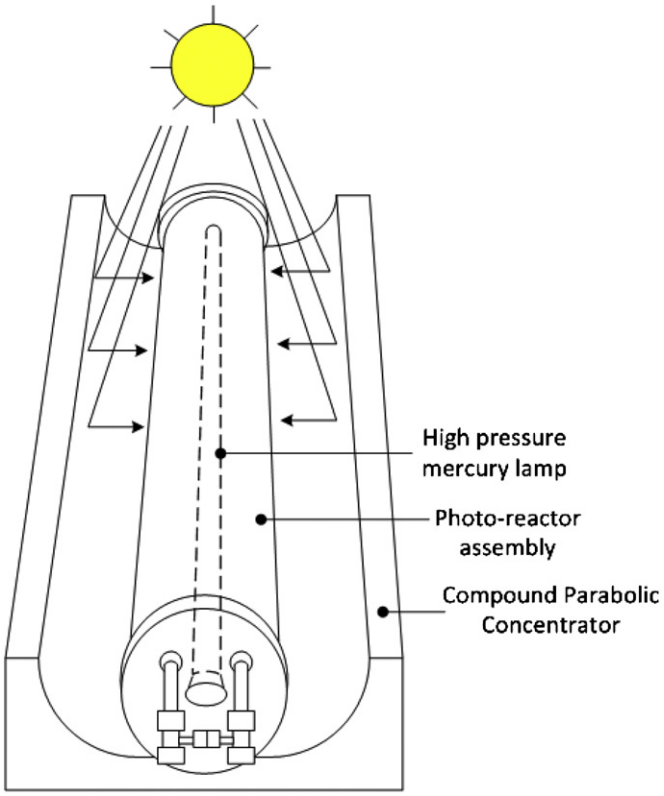

Fig. 1. Pilot-plant scale hybrid photo-reactor for continuous operation, under sunlight and artificial illumination.

The Nafion membrane was boiled in HNO_3 solution, and then rinsed with de-ionized water again prior to application. The compartments of the connected twin reactor were filled with an aqueous solution containing Fe^{3+}/Fe^{2+} as the electron-transfer mediator. In this way, hydrogen and oxygen can be generated separately. The average production rate of H_2 and O_2 was 0.71 and 0.35 mmol g^{-1} h^{-1}, respectively.

Yan et al. (2011) designed a dual-bed system to produce hydrogen through photocatalytic water splitting. The system was comprised of a photocatalytic reaction bed and a regeneration bed. Aqueous KI solution and Pt-loaded TiO_2 constituted the photocatalytic reaction bed where hydrogen was produced. The hole scavenger iodide ion was oxidized into I_2. The effluent containing I_2 from the photocatalytic bed entered the regeneration bed and passed through a Cu_2O layer where I_2 was reduced to I^-. The regeneration bed effluent was then recycled to the photocatalytic reaction bed.

With respect to the reaction system, most traditional reactors can only operate in a batch mode. The sacrificial agent is often irreversibly consumed. In this paper, a new design of a dual cell photocatalytic system is introduced, where photocatalytic hydrogen production occurs on one manifold and the oxygen evolution occurs on another manifold. This design leads to the formation of a continuous reaction system with a stable hydrogen production rate. For the production of hydrogen, development of an efficient solar light concentrator is a key issue because solar light is diffused and it has a relatively low energy intensity. A Compound Parabolic Concentrator (CPC) is analyzed for the sunlight-driven hydrogen production system.

Numerous studies on photochemical production of hydrogen have focused on the development of photocatalytic materials. Relatively few have examined thermodynamic studies of photocatalytic conversion of light energy in terms of energy and exergy efficiencies (Baniasadi et al., 2011). Currently, there exist several different approaches to the exergy analysis, i.e., Moran and Shapiro (1992), Bejan (1997). This paper examines the design of a solar photocatalytic hydrogen production reactor and the results based on energy and exergy efficiencies will be presented. The efficiency analysis is based on experimental data of $Cd_{1-x}Zn_xS$ solid solution photocatalyst (Jing et al., 2010) and supramolecular complexes $[\{(bpy)_2Ru(dpp)\}_2 2RhBr_2](PF_6)_5$ (White et al., 2011).

2. System description

A photo-catalytic reactor activated by sunlight and UV–visible lamps capable of continuous operation under real process conditions is considered for scale-up purposes. Fig. 1 shows an assembly of a hybridized photo-catalysis reactor that utilizes

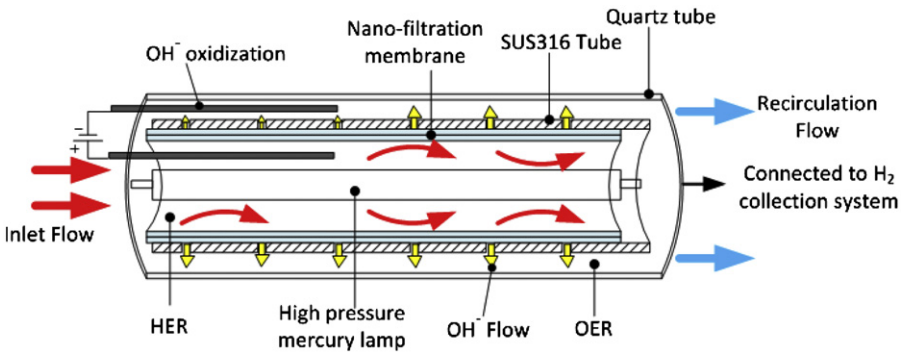

Fig. 2. Schematic of hybrid photo-reactor.