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Review (Special Issue of Photocatalysis for Solar Fuels)

Slow photons for solar fuels

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ABSTRACT

Converting solar energy into hydrogen and hydrocarbon fuels through photocatalytic H_2 production and CO_2 photoreduction is a highly promising approach to address growing demand for clean and renewable energy resources. However, solar-to-fuel conversion efficiencies of current photocatalysts are not sufficient to meet commercial requirements. The narrow window of solar energy that can be used has been identified as a key reason behind such low photocatalytic reaction efficiencies. The use of photonic crystals, formed from multiple material components, has been demonstrated to be an effective way of improving light harvesting. Within these nanostructures, the slow-photon effect, a manifestation of light-propagation control, considerably enhances the interaction between light and the semiconductor components. This article reviews recent developments in the applications of photonic crystals to photocatalytic H_2 production and CO_2 reduction based on slow photons. These advances show great promise for improving light harvesting in solar-energy conversion technologies.

1. Introduction

Human civilization is powered mainly by fossil fuels such as oil, coal, and natural gas. However, the combustion of these fuels causes environmental pollution and considerable CO_2 emissions. Solar power is widely recognized as a promising alternative to fossil-fuel-based energy sources. Considerable efforts have been made in the study, design, and synthesis of novel materials that can convert solar energy into heat, electricity, and chemical energy [1–4]. One such strategy is photocatalytic splitting of water molecules to generate hydrogen or to drive the reduction of CO_2 into valuable hydrocarbon fuels [5–8]. Currently, a myriad of materials has been shown to be potential candidates for such photocatalytic reactions. However, owing to limited light absorption and high rates of charge carrier recombination, the conversion efficiencies of current photocatalysts remain too low to meet commercial requirements. To enhance light harvesting, one important approach is to improve the interaction of light with the semiconductor, by manipulating light propagation in the various material structures. For instance, multiple scattering can be used to induce more photons to be absorbed under given incident light conditions [9,10]. Random scattering by large particles [11] or spherical voids [12] has also been applied in dye-sensitized solar cells. Furthermore, hierarchically structured porous materials provide interconnected porosity at different length scales, which is favorable for light harvesting [13–15]. Photonic crystals are formed by specific periodic arrangements of die-

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lectric materials, which have a unique role in regulating light, through light reflection, scattering, and the slow photon effect. The phenomena allow control over light propagation in the medium structure.

Photonic crystals are the best materials devised for light manipulation. Several papers have reviewed photochemical applications of photonic crystals, focused mainly on photocatalysis [14,16–18] and photovoltaics [14,17]. The slow photon effect has also been reviewed from the viewpoint of photocatalytic degradation [14,16]. In this review, we discuss both theoretically and experimentally the importance of the slow-photon effect in light-harvesting enhancement and its applications in solar-to-fuel energy conversion, i.e., photocatalytic H_2 production and CO_2 photoreduction. The photoreactivity enhancement of slow photons is highlighted and we discuss the potential for making considerable improvements to light harvesting through several strategies, which are likely to attract attention in the near future.

2. Photonic crystals and slow photons

Photonic crystals are periodic ordered structures in space composed of two or more materials with different dielectric constants. When light propagates inside a photonic crystal, the periodic Bragg scattering modulates light to form a photonic band gap (PBG), which is analogous to the electronic bandgap in semiconductor materials. In photonic crystals, light with certain frequencies is forbidden from propagating owing to the photonic stop band arising from the periodic modulation of the refractive index [19,20]. Slow light propagation near this stop band is a unique property of photonic crystals, and is an important principle for enhancing solar energy conversion efficiency [17,21,22]. As illustrated in Fig. 1, at the lower photon energy edge (red edge) of the photonic bandgap, the light standing wave peaks are primarily localized in the high refractive index sections of the photonic crystal, whereas at the higher photon energy edge (blue edge), the standing wave peaks are localized in the low refractive index sections [23]. This mechanism provides photonic crystals with the ability to manipulate light in a unique manner. Most importantly, at both the blue and red edges of the photonic bandgap, vanishing group velocity is observed. Photons with reduced group velocity are termed “slow photons” or “slow light” [14,23].

The slow-photon effect has been demonstrated, both theoretically and experimentally to be a promising solution for increasing light absorption in semiconductors by extending the residence time of photons in the material. When the electronic bandgap of the material and either the red edge or the blue edge of the photonic bandgap of the structure overlap in the frequency (wavelength) domain, slow photons are expected to improve light harvesting. Irradiation at a photon energy related to the structured material means that slow photons on the edges of the photonic bandgap ensure a longer presence of that energy within the structure, and the electronic bandgap allows the photon energy to be transferred to electrons and holes [14]. Coordination of these three phenomena is essential to extracting the benefits of slow photons for solar energy harvesting, e.g. photocatalytic degradation [18,24–27] and solar cells [23,28–30]. There are also conventional uses in lasers [31–34] and some other optical applications [35–39]. In the following sections, we survey the properties of photonic crystal materials and give examples of their applications to solar-to-fuel conversion based on slow photons (mainly photocatalytic H_2 production and CO_2 photoreduction).

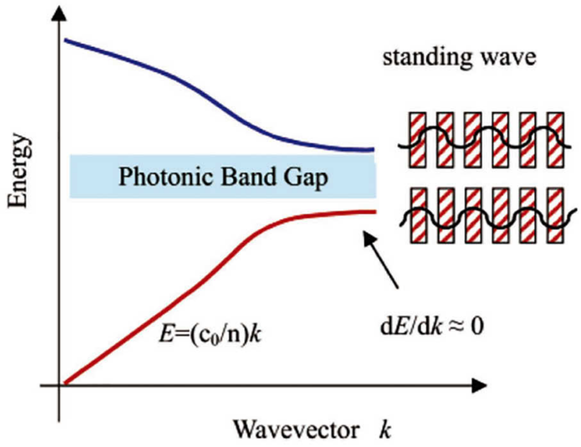

Fig. 1. Simplified photonic band structure of a photonic crystal. Near the Brillouin zone center, light travels with velocity c_0/n, where c_0 is the speed of light in a vacuum, and n is the average refractive index. At photon energies approaching the full bandgap or a stop band from the red side, the group velocity of light decreases and light can be increasingly described as a sinusoidal standing wave that has its highest amplitude in the high refractive index part of the structure. At energies above the bandgap or stop band, the standing wave is predominantly localized in the low refractive index part of the photonic crystal, i.e., in the air voids. Reproduced with permission [23]. (Copyright 2003 American Chemical Society Publishing Group).

3. Solar-to-H_2 energy conversion

Energy and environmental problems are well-known currently issues. Hydrogen fuel is a clean energy source that could provide the ultimate solution to many pollution problems. In particular, hydrogen evolution from water splitting powered by renewable solar energy represents a promising but challenging method to a clean, sustainable and affordable energy system. In this review, photocatalysts are structured into photonic crystal architectures to maximize the usage and conversion of light energy. Photonic crystal segments show a great capacity for light harvesting owing to the slow photon enhancement at the stop band edge and multiple scatterings among the segments.

Since the pioneering work of Fujishima and Honda in 1972, photocatalytic water splitting to produce H_2 using solar energy as the driving force has drawn considerable attention [5,8]. Generally, there are two configurations of photoconversion systems for water splitting. The first configuration of the photocatalytic system involves a suspension of the photonic crystal particles in a solvent [40,41]. This kind of system is made up of simple devices and accessible photocatalysts, where the driving force for water splitting comes entirely from solar energy. The reduction and oxidation reactions occur at different surface