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Enhancement of photoinduced hydrogen production from irradiated Pt/TiO$_2$ suspensions with simultaneous degradation of azo-dyes

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Abstract

The production of hydrogen from aqueous Pt/TiO$_2$ suspensions illuminated with UV–vis light has been examined in the absence and in presence of azo-dyes in solution. The effects of operational variables, including dye concentration, solution pH and temperature, on the rate of hydrogen production were investigated. It has been found that deposition of Pt (0.5 wt.%) on the semiconductor surface results in an increase of the H$_2$ production rate, which goes through a maximum with time of irradiation and then drops to steady-state values comparable to those obtained over bare TiO$_2$. Both, maximum and steady-state rates obtained over Pt/TiO$_2$ suspensions were found to increase with increasing solution pH and temperature. Addition of small quantities of azo-dyes in solution results in significantly enhanced rates of H$_2$ production for a period which depends on dye concentration, solution pH and, to a lesser extent, solution temperature. It is proposed that the dye acts as a scavenger of photogenerated oxidizing species while it is degraded toward CO$_2$ and inorganic ions. When complete mineralization is achieved, oxygen can no longer be removed from the photocatalyst surface and the rate drops to steady-state values, comparable to those obtained in the absence of azo-dye in solution. The amount of additional H$_2$ produced is directly proportional to the amount of dye added in the solution. The rate increases with increasing solution pH, where dye degradation is faster, indicating that the process is limited by the rate of consumption of photogenerated oxygen. It is concluded that, under certain experimental conditions, it is possible to obtain significantly enhanced rates of photoinduced hydrogen production from Pt/TiO$_2$ suspensions with simultaneous mineralization of azo-dyes. The process could be used for combined production of fuel H$_2$ and degradation of organic pollutants present in water.

Keywords: Photocatalysis; Splitting of water; Hydrogen production; Sacrificial agent; Azo-dye; Platinum; Titanium dioxide

1. Introduction

Photocatalysis on semiconductor surfaces, mainly titanium dioxide (TiO$_2$), has attracted considerable attention in recent years as a potential means for the mineralization of organic pollutants present in water and wastewater [1–4] as well as for the direct conversion and storage of solar energy [3–11]. One of the most widely investigated routes in the latter field of research is the photoinduced production of H$_2$ from decomposition of water [3–11]. The reaction may take place over n-type semiconductors, such as TiO$_2$, SrTiO$_3$ and CdS, illuminated with photons of energy equal to or higher than that of their bandgap energy (E_{bg}):

$$H_2O \xrightarrow[\text{semiconductor}]{h\nu\ \geq\ E_{bg}} H_2 + \tfrac{1}{2}O_2 \qquad (1)$$

When a n-type semiconductor is immersed in water, charge transfer occurs at the interface, and an electric field is formed in the direction from the bulk of the semiconductor toward the interface [7]. If an electron–hole pair is formed in this region by photoexcitation of the semiconductor, the electron moves toward the bulk of the material and the hole moves toward the surface, thus spontaneous separation of charge carriers is accomplished. Depending on the positions of the valence band (VB) and the conduction band (CB) of the semiconductor with respect to the redox potential of water, reduction, oxidation or splitting of H$_2$O may take place. In particular,

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production of hydrogen may occur when the potential of the conduction band (E_{CB}) is lower than $E(H^+/H_2)$ (0 V at pH 0). Accordingly, production of oxygen may take place only if the potential of the valence band (E_{VB}) is higher than $E(O_2/H_2O)$ (1.23 V at pH 0) [11]:

$$\text{semiconductor} \xrightarrow{h\nu\ \geq\ E_{bg}} e^- + h^+ \quad (2)$$

$$2e^- + 2H^+ \rightarrow H_2 \quad \text{when} \quad E_{CB} < E(H^+/H_2) \quad (3)$$

$$2h^+ + H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ \quad \text{when} \quad E_{VB} > E(O_2/H_2O) \quad (4)$$

Therefore, semiconductors with band energy levels which straddle the hydrogen and oxygen evolution potentials, such as TiO_2 ($E_{bg} = 3.2$ eV), ZnO ($E_{bg} = 3.2$ eV), SiC ($E_{bg} = 3.0$ eV), CdS ($E_{bg} = 2.25$ eV) and CdSe ($E_{bg} = 1.7$ eV) are, in principle, able to split water. Semiconductors like SnO_2 ($E_{bg} = 3.8$ eV), WO_3 ($E_{bg} = 2.6$ eV) and Fe_2O_3 ($E_{bg} = 2.1$ eV) generate photoelectrons with relatively low reducing ability, and therefore cannot reduce but only oxidize water (Eq. (4)), while other materials, including GaS ($E_{bg} = 1.4$ eV) can only reduce water to produce H_2 (Eq. (3)).

In addition to suitable positions of valence and conduction band energy levels, potential semiconductor materials for solar energy conversion should be characterized by relatively low bandgap energies, in order to be able to absorb sunlight efficiently. In this respect, low bandgap, non-oxide semiconductors, such as CdS, GaS and CdSe are more suitable than large bandgap, oxide, semiconductors. However, the former group of materials are often characterized by low chemical and/or photochemical stability [7,11], rendering them, in principle, not useful for practical applications.

Among the various semiconductors which have been studied for the photoinduced splitting of water, titanium dioxide (TiO_2) has been intensively investigated following its use by Fuzishima and Honda [6] because of its favorable bandgap energy and flat band potential and because of its high chemical and photochemical stability, biological inertness and low cost. The major drawback is that TiO_2 can be excited by photons in the near-UV rather than the visible spectral region, and therefore can make use of less than 5% of the solar energy, which reaches the surface of the earth. In particular, the bandgap of anatase TiO_2 is 3.23 eV (384 nm) whereas that of rutile TiO_2 is 3.02 eV (410 nm) [4,11].

Numerous attempts have been made to improve the inherently low efficiency of TiO_2 in harvesting sunlight by shifting its spectral response into the visible, including doping of TiO_2 with a variety of cations [12–14], anions like nitrogen [15] or by chemical modification with carbon [16]. In all cases, the aim is to decrease the bandgap of the semiconductor or to introduce intra-bandgap states, both of which may result in enhanced visible absorption [4]. Extension of light absorption to longer wavelengths can also be achieved with the use of dye-sensitized TiO_2 systems [5,17,18].

An alternative way to improve the photocatalytic performance of TiO_2 is to increase its photoactivity in the near-UV portion of the spectrum by retarding the recombination of electrons and holes, which occurs in the nanosecond regime. In photoelectrochemical cells, this is done by application of an electric field at the electrode/electrolyte interface [7,19,20]. In particulate systems, a similar effect is imposed by deposition of noble metals on the photocatalyst surface. For example, dispersion of Pt on TiO_2 results in the formation of a Schottky barrier at the metal/semiconductor interface, which leads to a decrease in electron–hole recombination rate, as well as to a more efficient charge separation [21]. The role of the dispersed metal crystallites is to ‘‘pump’’ photogenerated electrons from the semiconductor and to increase the electron transfer rate to the adsorbed species, thus retarding the possibility of their recombination with holes. In addition, deposition of metal (e.g., Pt) and/or metal oxide (e.g., RuO_2) particles on TiO_2 improves reaction kinetics by decreasing the overpotentials for hydrogen and oxygen evolution, respectively [22,23].

Higher efficiencies for the photoinduced hydrogen production may be also achieved with the use of electron donors as sacrificial agents, which react irreversibly with photoinduced holes and/or photogenerated oxygen thereby suppressing the electron–hole recombination and/or the reverse reaction between O_2 and H_2 [8,23–26]. If this sacrificial agent is a pollutant present in water or wastewater, the overall process would be the enhancement of the H_2 production rate with simultaneous degradation of the organic substrate.

Photocatalytic cleavage of water in aqueous suspension over TiO_2-based photocatalysts has been studied in detail in this laboratory [12,27,28]. The effects of addition of Pt and/or RuO_2 on the photocatalyst surface, as well as the effects of various operating variables and of parameters related to the structure of the catalyst on the rate of H_2 production under UV illumination were investigated. It was found that the rate of H_2 production does not depend on the details of surface structure of Pt and is not sensitive to the surface area of the catalyst or to the method of preparation of the semiconductor. However, the efficiency of the photocatalytic process is significantly affected by the crystallographic structure of TiO_2, while the rate of H_2 production is strongly dependent on the pH of the solution [27].

On the other hand, the photocatalytic degradation of Acid Orange 7 (AO7) in aerated aqueous TiO_2 suspensions has also been the subject of detailed investigation in this laboratory [29–33]. It was shown that complete decolorization and substantial reduction of the chemical oxygen demand (COD) of the solution can be achieved with satisfactory rates with the use of optimal operational parameters. The photocatalytic reaction pathways have been examined in detail and a TiO_2-mediated photodegradation mechanism has been proposed on the basis of quantitative and qualitative determination of intermediate compounds [30–32].

The objective of the present study is to investigate the possibility of combining the above-mentioned reactions, i.e., water reduction and dye oxidation, into a single process characterized by enhanced hydrogen production rates and efficient dye degradation.