

Significance of pH measurements in photocatalytic splitting of water using 355 nm UV laser

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Abstract

The pH changes during the course of photocatalytic splitting of water significantly affect the band edges of the semiconductor and enhance or retard the rate of the splitting process. The effect of pH on photocatalytic activity in splitting of water over WO₃, TiO₂ (rutile) and NiO by using a monochromatic light source such as laser at 355 nm wavelength was studied for the first time. The mechanism of action of oxygen and metal ions (Fe³⁺ and Ag⁺) as electron capture agents was investigated on the basis of pH changes under illumination. It was observed that the pH changes measured during the course of reaction provides a deep insight of different processes occurring simultaneously in photocatalytic systems.

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1. Introduction

The pH of a system is a measure of the concentration of H⁺ ions and is considered as a valuable tool in evaluating the mechanisms of various inorganic and organic reactions. Heterogeneous photocatalysis is a developing field [1–14] in which the pH changes play a vital role when applied for water splitting. To oxidize water, the potential of valence band (V_{vb}) should be more positive than +1.23 V (H₂O/OH). The positions of both conduction and valence bands, in aqueous medium, are pH dependent and the change in the pH of the semiconductor/electrolyte system by one unit shifts the position of the flat-band potential (V_{fb}) of the semiconductor by 59 mV [1,3–5]. In other words, the change in the pH of the photocatalytic system shifts the position of valence band and conduction band edge, which in turn affects the ability of the

semiconductor to photo-oxidize or photo-reduce [15].

$$E_{vb} = E_{vb}^0 - 0.059 \text{ pH} \quad (1)$$

$$E_{cb} = E_{cb}^0 - 0.059 \text{ pH} \quad (2)$$

where E_{vb}^0 and E_{cb}^0 are the valence and conduction band potentials at zero pH.

The effect of “preset pH” on different processes especially photocatalytic degradation have been extensively studied and its impact on the mechanism of degradation have been discussed [16–24]. Various studies have been performed to investigate different processes under different pH values but less effort have been focused on measuring the pH changes during the course of a photocatalytic process and the effect of these changes on the processes occurring at the surface of the catalyst and bulk.

Keeping in view the significant effect of the shifting of the valence and conduction band edges due to pH changes during a photocatalytic process, the mechanism of photocatalytic splitting of water over WO₃, TiO₂ (rutile) and NiO by

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using a laser emitting at 355 nm wavelength has been studied in this paper for the first time. The pH changes under UV laser illumination were used for finger printing the action of oxygen and metal ions as electron capture agents, and the action of methanol as a hole-capture agent. It was observed that the pH changes measured during the course of reaction provides a deep insight of the processes occurring simultaneously in the photocatalytic splitting of water.

2. Experimental details

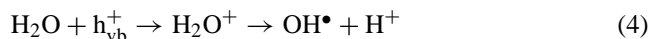
A schematic diagram of the experimental setup applied in this study is presented in Fig. 1, and is described in detail in earlier publications [25–28]. The pH changes in the solution during laser irradiation were measured using a pH meter that was calibrated by using the buffers of pH 4, 7 and 10. For pH measurements during water splitting, 300 mg of each catalyst (WO_3 , TiO_2 and NiO) was suspended in 60 ml of doubly distilled water and exposed to a 355 nm wavelength laser beam generated by the third harmonic of a Nd:YAG pulsed laser (Spectra Physics Model GCR 250). All experiments were performed at an optimal laser energy of 100 mJ per pulse, as discussed in detail elsewhere [26]. Argon gas was initially purged through the solution to remove the dissolved oxygen. For the pH measurements during water-splitting studies in the presence of metal ions, a 10 ppm solution of each metal ion was prepared by dissolving the stoichiometric amounts of metal nitrates in 1000 dm³ of doubly distilled water. For each experiment, 300 mg of the catalyst was suspended in 60 ml of the respective metal solutions. A 10 ppm concentration of each metal ion was chosen so as to minimize the optical effects such as self absorption by the metal ions. The pH measurement experiments in the presence of the hole capture agent (i.e., methanol) were performed by adding 10 μl of methanol in colloidal suspension of each catalyst. The pH changes in the presence of electron and hole capture agents

were performed by using 10 ppm solutions of the respective metal ions and 10 μl of methanol. To ensure reproducibility, all the experiments were performed in duplicate. All the experiments were performed at room temperature and atmospheric pressure.

3. Results and discussion

In this study, the role of pH changes during the course of illumination for the photocatalytic splitting of water over three catalysts, i.e., WO_3 , TiO_2 and NiO has been investigated. The choice of the photocatalysts (WO_3 , TiO_2 and NiO) was based on their stability in aqueous suspensions under laser illumination [27]. The laser photon energy of 355 nm (~ 3.5 eV) was in close agreement with the bandgap of semiconductor powders (2.8, 3.2 and 3.5 eV for WO_3 , TiO_2 and NiO , respectively). The valence and conduction band edge potentials of WO_3 , TiO_2 and NiO are +3.2, +2.70, +3.0 and +0.4, -0.4, -0.5 V, respectively [29–30].

When illuminated, H_2O splits into its components over the surface of a photocatalysts by donating the electrons to the photogenerated holes, with the formation of hydroxyl radicals (OH^\bullet) and H^+ ions as shown in Eqs. (1) and (2). This is possible when the valence band edge of the catalyst is positive than +1.23 V,



The combination of hydroxyl radicals produced because of water oxidation generates oxygen (Eq. (5)).



The capture of conduction band electrons by H^+ ions leads to the formation of hydrogen if the potential of the conduction

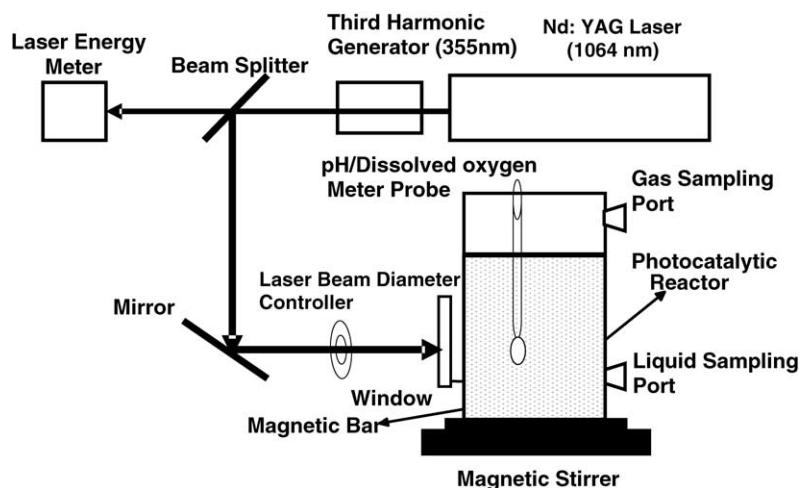


Fig. 1. Schematic diagram of the experimental setup for pH measurement applied for laser photocatalytic water splitting.

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