



Intensification of photocatalytic decomposition of water by ultrasound

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ABSTRACT

Photocatalysis of water with and without ultrasound was studied using rGO supported CdS catalyst utilizing visible light. A higher hydrogen production was observed when ultrasound was used. This is attributed to a faster removal of bubbles of hydrogen from the surface of photocatalyst due to the mechanical energy associated with ultrasound overcoming surface tension. It has been further reported that the rate of hydrogen production decreased with time due to reversible deactivation of catalyst. This has been attributed to decrease in rate of hydrogen desorption with time.

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1. Introduction

Photocatalysis of water to produce hydrogen utilizing solar radiation is a promising technology. Hydrogen, on burning, produces heat and is reformed into water. Therefore, the process becomes completely renewable and does not produce air pollutants like CO₂ or CO which are generated by burning of fossil fuels. However, for photocatalysis to become successful it is essential that an active and durable catalyst should be developed.

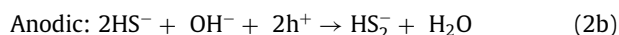
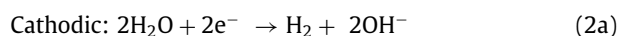
A large number of semiconductor photocatalysts have been reported in the literature [1–4]. They are mostly sulfide [5–7] or oxide [8–10] based catalysts. Recently reduced graphene oxide (rGO) supported cadmium sulphide (CdS) catalysts [11–15] have shown promise and therefore, extensive work is under progress to develop active rGO based CdS catalyst. In addition the design of a photoreactor which provides for an efficient capture of solar radiation is also a challenge. For the design of a photoreactor the kinetics of dissociation of water must be known. Surprisingly not much work has been reported in the literature on the mechanism and kinetics of the reaction. Working on CdS based catalysts with Na₂S alone or in combination with Na₂SO₃ as sacrificial agents, it has been reported that rate of hydrogen production declines after sometime and eventually becomes zero. The deactivation of catalyst was concluded to be the reason of fall in the hydrogen production rate. Kinetics studies have been reported in the literature but all have focused on initial rate determination and mechanism of the reaction. It has been also concluded that the rate limiting step is surface reaction related to an anodic type reaction [16–19]. The

overall activation energy was found to be 2.52 kcal/mol [17]. Sebate et al. [17] have proposed the following general steps in the photo-production of hydrogen from sulphide and sulphite mixtures:

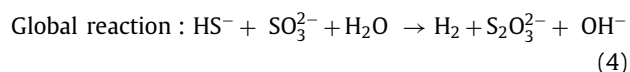
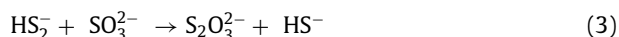
Step 1, absorption of photon:



Step 2, reaction on the catalyst surface:



Step 3, reaction in the liquid phase:



In an earlier work carried out in our laboratory with CdS based catalyst and sodium sulphide & sodium sulphite as sacrificial agents, a detailed kinetics study was reported [20]. The rate was found to be related to sulphide ions adsorbed on the surface of CdS. The decrease in the rate of H₂ production was concluded to be due to the deactivation of catalyst by the product hydrogen itself. A power law type of rate expression for hydrogen was proposed which took into account the deactivation of the catalyst also.

Further, a few work have been reported in literature on the synergetic effect of ultrasound and photocatalytic reaction system in removal of water pollutants [21–23] and hydrogen production [24,25]. Gentili et al. [26] have reported that the combined effect

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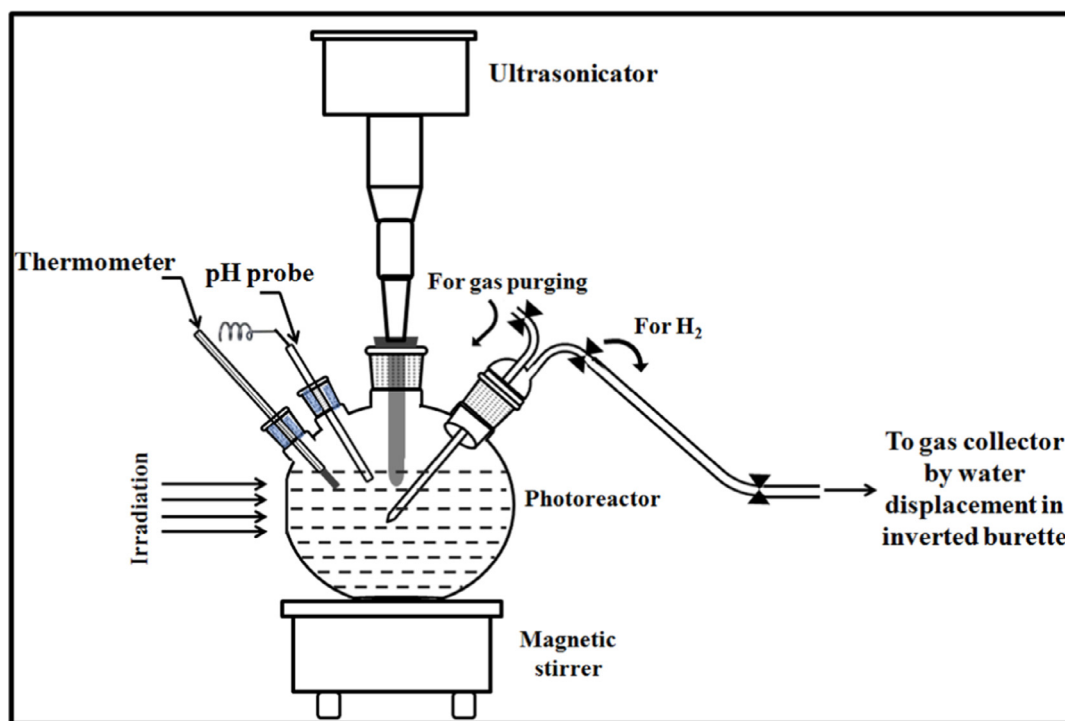


Fig. 1. The schematic view of the photoreactor for photocatalysis with ultrasound.

of electromagnetic (of light) and mechanical (of ultrasound) waves enhanced mass transport and consequently rate. Hisashi et al. [27], and Shao et al. [28] have reported that sonication alone may result into decomposition of water: $2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{O}_2$. Shah et al. [29], and Chakna et al. [30] have reported formation of OH^\cdot radicals by sonolysis through transient collapse of cavitation bubbles formed by ultrasound. Suslick et al. [31], Hilgenfeldt et al. [32], and Ashokkumar et al. [33] have concluded that transient cavitation creates intense local energy concentration on extremely short-temporal and spatial scale which also emits light during transient collapse. Recently, Chakma et al. [34] have reported adverse effect of ultrasound on the oxidation of dye by photocatalysis. They reported that shock wave generated by cavitations bubbles resulted into desorption of dye molecules adsorbed on the surface of photocatalyst.

In order to investigate the possibility of enhancement of photocatalytic hydrogen production rate by ultrasound, we carried out experiments with the CdS based catalyst [35] and Na_2S & Na_2SO_3 as sacrificial agents. The results are presented in this paper. This paper also reports results of our analysis on the decrease in hydrogen production rate with time.

2. Experimental

2.1. Catalyst

The catalyst was CdS supported on rGO with a weight ratio of 1:2 (CdS:rGO). The catalyst was prepared by impregnation followed by a gas-solid reaction. Details are given elsewhere [35].

2.2. Experimental set-up

The experimental setup and procedure were same as given in our earlier paper [35]. The reactor was typically a four necked flat bottomed flask with a vertical surface ~ 7 cm was made flat for light to fall. Gas outlet of the reactor was connected to an inverted burette. The only modification was (as shown in Fig. 1) that

it had a provision to insert an ultrasonic horn. Its tip was inside the electrolyte up to a depth 5 cm. The tip was made of stainless steel (SS304) having a diameter of 4 mm. The horn was connected to PZT transducer type ultrasound generator capable of generating ultrasound of 20 kHz frequency at different input powers from 10 to 40 W. One gram of catalyst was suspended in 250 mL of aqueous solution of concentration 4.0 and 10.0 mM with the respect of Na_2SO_3 and Na_2S , respectively. The pH was maintained at 8.6 during the experimentation by adding required amount of acetic acid and NaOH. Nitrogen gas was purged for 1 h prior to irradiation to remove dissolved gases from this solution. The gas evolved by photocatalytic reaction was collected continuously in an inverted burette by a water displacement technique. It ensured that the pressure inside the reactor was near atmospheric pressure. The gas collected in the burette was analyzed by a gas chromatograph using a 5 Å molecular sieve column and thermal conductivity detector. The results showed that the evolved gas was pure hydrogen. Whenever, the experiment was carried out with ultrasound, the magnetic stirrer was put off because the particles remained in suspension due to effect of ultrasound.

3. Results and discussion

The results of hydrogen production without ultrasound for repeated runs are shown in Fig. 2(a). Hydrogen production rates were also calculated at different duration by measuring the slop of curves of Fig. 2(a) and are shown in Fig. 2(b). Before each run, the liquid was purged with N_2 gas for 1 h. Further at end of any run the light was put off and the liquid with catalyst was kept in dark for more than 6 h and also solution was replenished with requisite amounts as calculated by the stoichiometric equation (Eq. (4)) of sodium sulphide and sodium sulphite.

It is observed from the figure that with duration of run the hydrogen production rate was constant for initial 30 min and subsequently started falling down and became negligible after 90 min for all the four runs. It is further observed that if the liquid and catalyst are kept in dark for a sufficient long period of time and

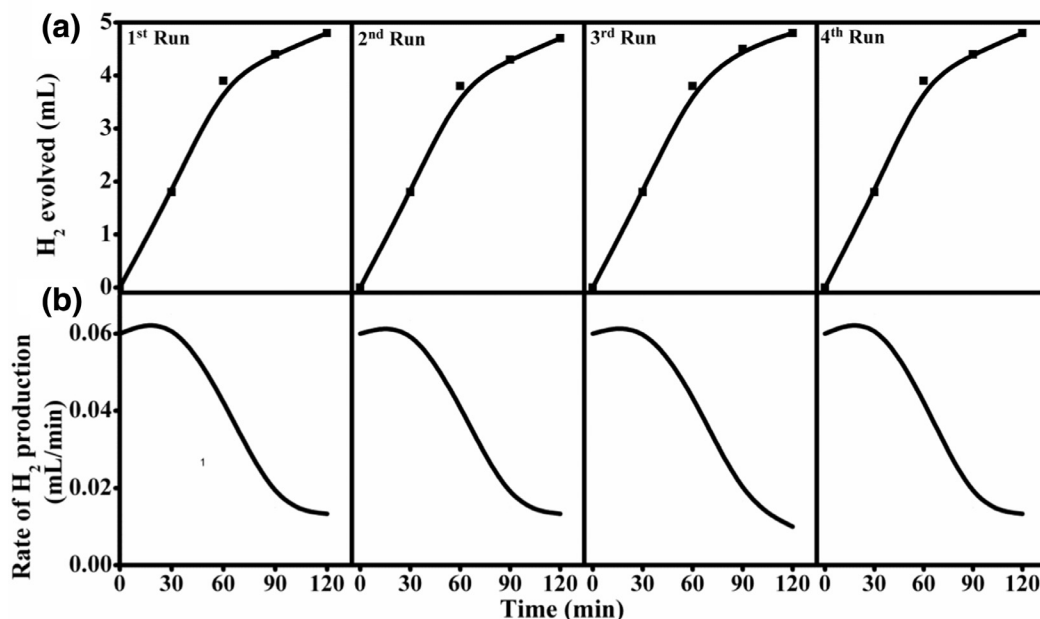


Fig. 2. (a) Hydrogen evolved vs time, (b) hydrogen production rate without ultrasound.

the liquid is purged with N_2 prior to the start of experiment, the hydrogen production rate was fully regained. In the earlier work in our laboratory, same observations were reported and it was concluded that the product hydrogen caused the reversible deactivation of catalyst. The mechanism of deactivation was not explained. It should also be noted that the drop in concentration of S^{2-} in each run was of the order of 10%–15% only. Clearly 10%–15% decrease in concentration of S^{2-} may not be attributed to ~90% decreases in hydrogen production rate. Further, polysulphides are known to deactivate CdS but due to presence of sulphite ions in the liquid, the polysulphide which is formed, reacts with sulphite ions and thiosulphate. In addition, since the deactivation was completely reversible, the possibility of deactivation due to accumulation of polysulphide was ruled out. Therefore, in the present work also, we attribute the decrease in rate to reversible deactivation of catalyst by hydrogen.

Further experiments were carried out to study the effect of ultrasound on hydrogen production. The experimental details remained the same as given earlier for photocatalysis without ultrasound. The only difference was that the magnetic stirrer was not used to keep particles suspended and an ultrasonic horn was introduced with its tip immersed in liquid and it produced ultrasound waves of frequency 20 kHz. The input power of ultrasound was 35 W. The ultrasonic wave was found to be sufficient to keep the particles suspended in the liquid. Experiments were carried out in dark and no hydrogen production was observed. Since further, no oxygen was detected in the gas evolved therefore, the possibility of dissociation of water by ultrasound was ruled out. Thus, the hydrogen gas evolve was by photocatalytic dissociation of water only. The result is shown in Fig. 3. It is observed that the total amount of hydrogen produced increased to 8 mL when photocatalysis was carried out in presence of ultrasound in comparison to 4.8 mL when photocatalysis was not combined with ultrasound. Literature reports that ultrasound may enhance the rate due to (a) formation of reactive intermediates (like OH^\cdot), (b) rise in temperature and thus making thermochemical reaction faster, (c) making more surface of catalyst available for a greater absorption of light and (d) enhanced transport of intermediate of product for the surface to bulk.

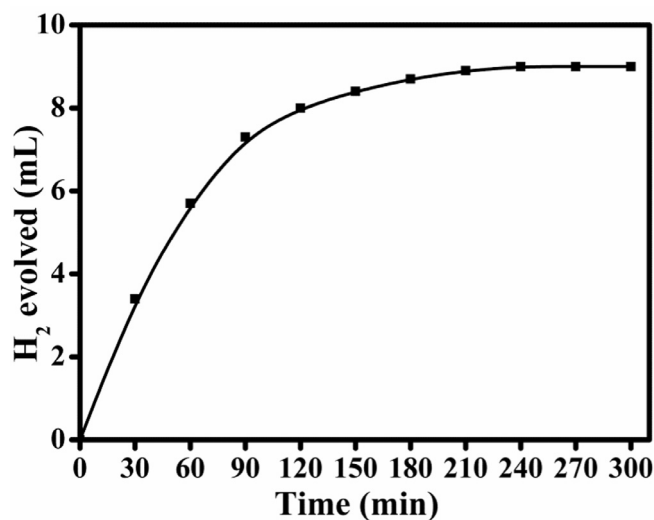


Fig. 3. Hydrogen evolved vs time with ultrasound (Input power 35 W).

As mentioned earlier, since no oxygen was detached in the evolved gas, the formation of reactive species as mentioned in the literature [29,30] cannot be the reason for the observed enhancement. Further, ~200 mesh size catalyst was used in all the experiments and which were well agitated. Therefore, creation of new surface area and a greater absorption of light may not be important. Experiments were also carried out with different input energies of ultrasound. The results are shown in Fig. 5. It is observed that beyond a power input of 35 W, there was no enhancement in total hydrogen production. Therefore, a greater absorption of light due to ultrasound may not explain the observed enhanced rate due to ultrasound.

Effect of rise in temperature due to ultrasound was also investigated. It was observed that when ultrasound was employed during photocatalysis of water, the temperature of the photoreactor rose from 299 to 318 K. To ascertain the effect of temperature on photocatalysis of water, experiment was carried out maintaining the

temperature of reactor at 318 K in the absence of ultrasound. The volume of hydrogen production was ~10% higher than that obtained when the temperature did not maintain constant. It is in order to mention that Sebate et al. [17] have studied the kinetics of photocatalysis of water for hydrogen production from sulphide and sulphite waste streams. They have reported activation energy 2.52 kcal/mol. Accordingly, a calculation shows that enhancement in rate of production when temperature rises from 299 to 318 K cannot be more than 28%. We have observed ~70% enhancement in the rate of photocatalytic hydrogen production when assisted by ultrasound. Therefore, we conclude that the rise in temperature does not have significant effect on photocatalytic hydrogen production rate. We conclude that the mechanical energy of the sound wave or that of shock wave created by collapse of bubbles formed due to cavitations were responsible for the increasing in the hydrogen production rate.

The overall photocatalytic process will consist of the following steps:

- (a) Absorption of a photon
- (b) Adsorption of reactants on the surface of catalyst
- (c) Reaction on the surface of catalyst
- (d) Desorption of intermediates and (or) products
- (e) Transfer of intermediate and (or) products from surface to bulk of the liquid
- (f) Subsequent liquid phase reaction

The mechanical energy of ultrasound can enhance the transfer of intermediates and products for surface to bulk of liquid. Drawing an analogy with boiling phenomenon on a heated plate, we studied the possible role of bubble formation and its detachment from the catalyst surface. Since surface tension plays an important role in the bubble detachment, experiments were further carried out to study the effect of surfactant on hydrogen production rate. A sulphur based surfactant (sodium dodecyl sulphate 5 mmol/L) was mixed in the electrolyte solution containing catalyst and hydrogen production was measured for (a) photocatalysis alone and (b) photocatalysis with ultrasound. A sulphur based surfactant was used because the catalyst was sulphide and electrolyte was also solution of sulphide and sulphite. The results are shown in Fig. 6(a) and 6(b), respectively. It is observed that in the case of photocatalysis alone the amount of hydrogen evolved increases from 4.8 mL to 5.4 mL in 2 h. Whereas no such increase was observed in case of photocatalysis with ultrasound. Surfactant reduces the surface tension. Thus the lowering of surface tension has increased the rate of hydrogen production when no ultrasound was used.

The above observations can be explained on the basis of bubble growth and its detachment from the surface. After the desorption of product hydrogen from the active sites of photocatalyst, the hydrogen will remain on the surface of catalyst due to various forces acting on it. The forces acting on a bubble on any solid surface which cause detachment of bubble are buoyancy, shear lift and contact pressure forces whereas forces opposing detachment are drag force and force due to surface tension. The forces are depicted in Fig. 7 [36]. At a certain critical size of the bubble, the forces causing detachment overcome the forces opposing the same and the bubble gets detached from the surface. A schematic representation of surface of the photocatalyst is shown in Fig. 8. Considering only surface tension force and buoyancy force, Fritz [37] developed an equation of bubble departing diameter (d):

$$d \text{ (mm)} = 0.208\theta \left[\frac{\sigma}{g(\rho_L - \sigma_g)} \right]^{1/2} \quad (5)$$

Where, σ is the surface tension, θ is contact angle, g is gravitational acceleration and ρ_L & ρ_g are density of liquid and gas, respectively.

Similarly, during the photocatalytic reaction the hydrogen gas which is formed on the surface will remain on the surface till its bubble grows to critical size (departing size). In such a situation, a fraction of surface of the photocatalyst will be occupied by hydrogen and thus become unavailable for the adsorption of reactant (HS^-). As shown in the Fig. 7 the force due to surface tension prevents bubble detachment and critical size of departing bubble is proportional to $(\text{surface tension})^{1/2}$. Hence, any reduction in surface tension will reduce the critical size of departing bubble and will facilitate detachment of bubble of smaller size. And thus providing a larger fraction of catalyst surface for adsorption and reaction with an enhancement in rate. Therefore, when the experiment was carried out by adding a surfactant in the liquid, the enhanced hydrogen production rate was observed when the photocatalysis was carried out in absence of ultrasound waves. However in presence of ultrasound waves, no such enhancement was observed. It is attributed to the fact that the mechanical energy of ultrasound waves destabilize the bubbles on the surface and bubbles of much smaller sizes are released. A schematic representation of the bubble detachment from the surface of photocatalyst in presence of ultrasound is shown in Fig. 9. Therefore, reduction in surface tension did not have (Fig. 6b) any noticeable effect on bubble departure size and hydrogen production rate when photocatalysis was carried out in the presence of ultrasound.

Thus, the observed increase in the rate of hydrogen production by photocatalysis assisted by ultrasound is due to the faster detachment of bubbles from the surface by overcoming the surface tension force with the help of mechanical energy of ultrasound wave. As reported earlier the rate increased with the increase of input power of ultrasonication but beyond a 35 W power, no further enhancement was observed. It is clear that if bubbles detach as soon as they are formed. The overall process shall be governed by the rate of generation of hydrogen and the effect of ultrasound wave beyond a certain input of power shall not lead to any further enhancement. In addition to the mechanical energy of ultrasound wave, mechanical energy of shock wave due to collapse of bubbles formed by cavitations may also destabilize the hydrogen bubbles on the surface. Thus the higher rate of transfer of hydrogen due to the mechanical energy of ultrasound has been attributed to the enhancement of hydrogen production rate when photocatalysis was carried out in presence of ultrasound.

It has been further observed and as reported earlier that the rate of hydrogen production drops down with time in both the conditions, i.e. photocatalysis with and without ultrasound (refer Figs. 2b and 4, respectively). It was further observed, as stated earlier (Fig. 2) that this deactivation of catalyst was completely reversible. Experiments were further carried out where prior to the start of the experiment the electrolyte solution was saturated with hydrogen by purging hydrogen gas in the solution containing catalyst. Result of the experiments is shown in Fig. 10. For comparison, the result of experiment when nitrogen gas was purged is also shown in the Figure. It is observed that the total hydrogen production as well as rate both has decreased drastically. The total hydrogen production was only 1 mL in 2 h when the liquid was saturated with hydrogen in comparison to 4.8 mL when electrolyte was purged with N_2 gas prior to experiment. The result clearly shows that the presence of hydrogen in the system adversely affects the rate. The similar observation has been reported in literature [20]. The kinetic steps of the reaction consist: (a) adsorption of reactants, (b) anodic and cathodic reactions, and (c) desorption of products including hydrogen ((Eqs. (1–4)). When the desorption of hydrogen is the rate determining step, its rate of desorption and consequently the overall rate of hydrogen products shall be affected by the presence of hydrogen in the system. Any increase in the concentration of hydrogen will lower the rate of desorption of hydrogen and consequently rate of hydrogen production. Therefore,

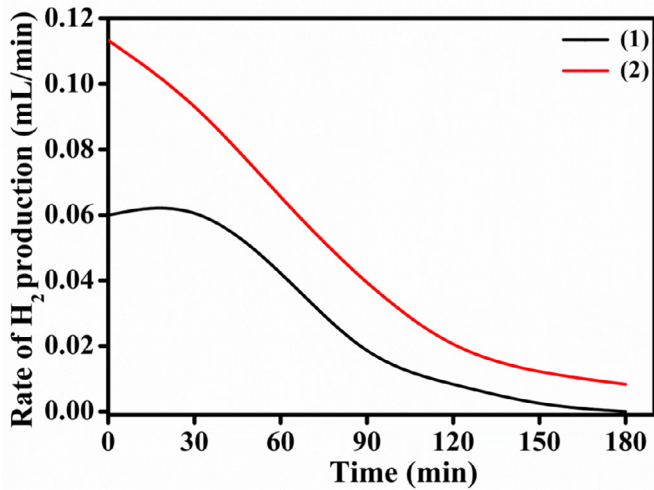


Fig. 4. Hydrogen production rate (1) without ultrasound, (2) with ultrasound (Input power 35 W).

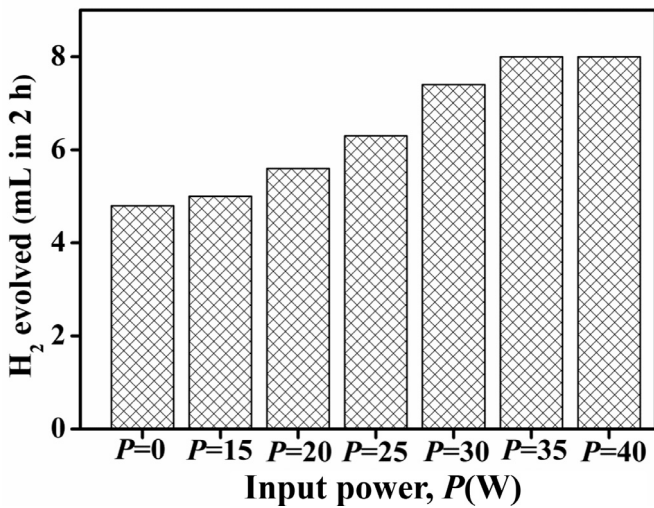


Fig. 5. Hydrogen evolved (in 2 h) vs ultrasonication power applied in photocatalytic reaction with solar radiation.

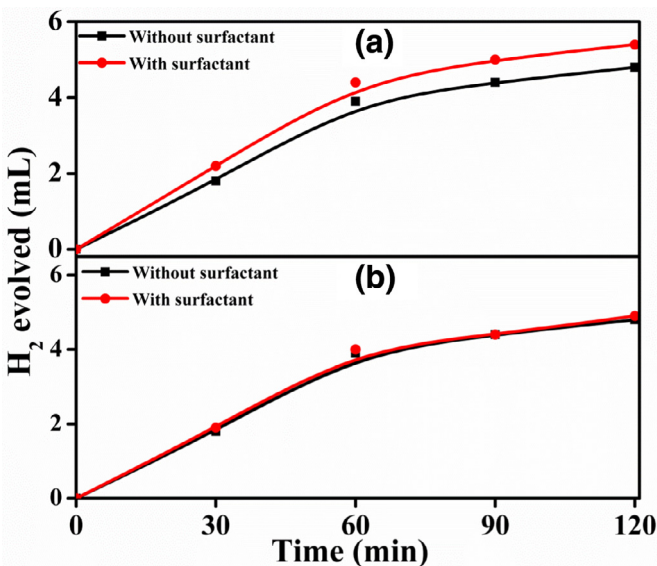


Fig. 6. Effect of surfactant-hydrogen evolved by photocatalysis. (a) without ultrasound, (b) with ultrasound.

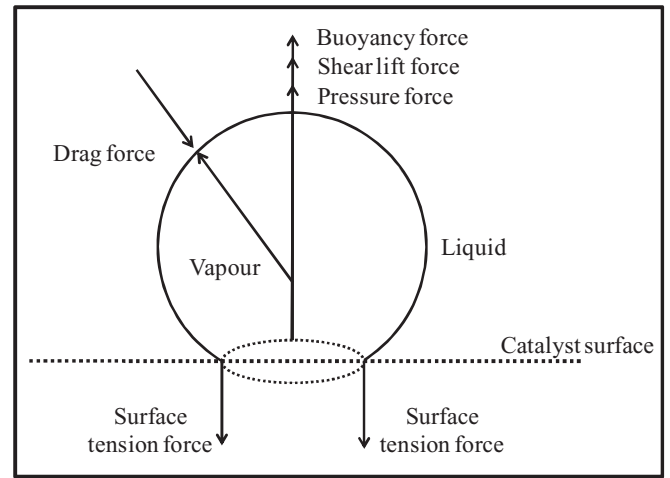


Fig. 7. Forces on single bubble on solid surface [33].

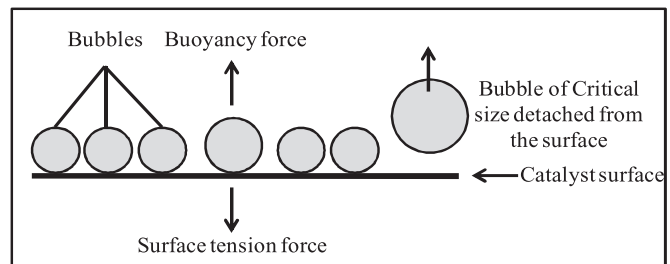


Fig. 8. Schematic representation of hydrogen bubbles on catalyst surface without ultrasound.

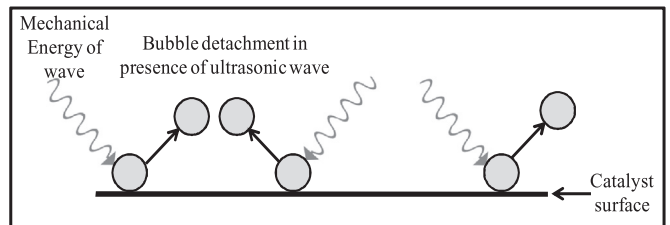


Fig. 9. Schematic representation of hydrogen bubbles on catalyst surface with ultrasound.

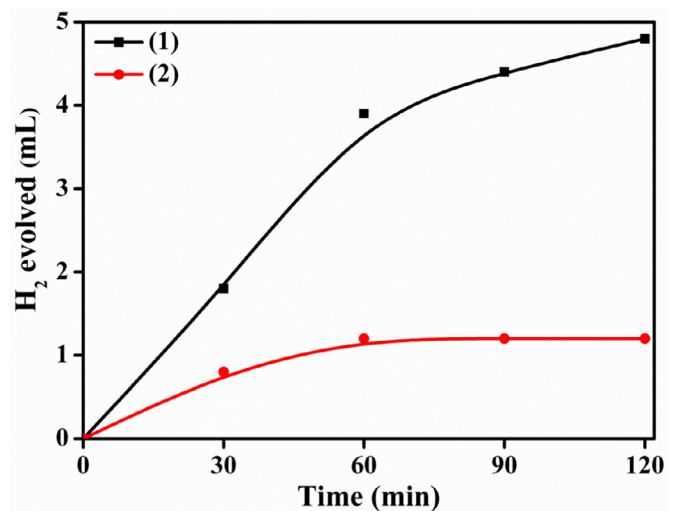


Fig. 10. Hydrogen evolved (without ultrasound). (1) Electrolyte was purged with N₂ for 1 h; (2) Electrolyte was purged with H₂ for 2 h.

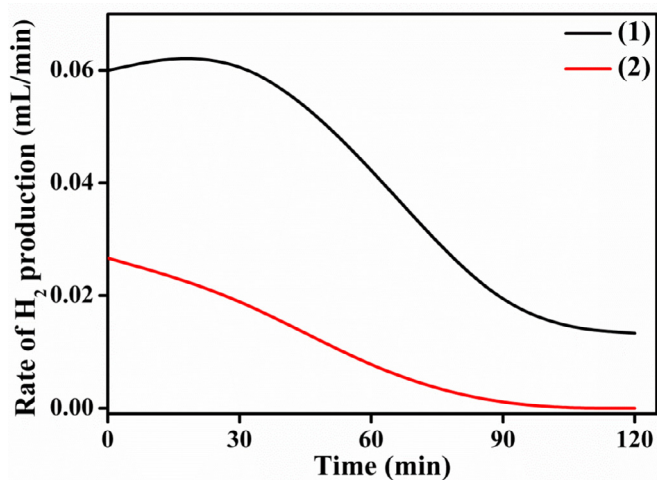


Fig. 11. Hydrogen production rate (without ultrasound). (1) Electrolyte was purged with N_2 for 1 h; (2) Electrolyte was purged with H_2 for 2 h.

the decrease in rate of hydrogen production is attributed to gradual built up of hydrogen in the system with time causing decrease in rate of desorption of hydrogen and consequently hydrogen production rate with time. It also explains the observation that hydrogen production rate was fully regained when the system was purged with nitrogen and therefore the deactivation of catalyst was completely reversible. Thus, it may be summarized that the photocatalytic decomposition of water for hydrogen production is affected by both transfer of hydrogen from the surface of catalyst to the bulk and desorption of hydrogen from the active sites. Ultrasound enhances the transfer of hydrogen only (Fig. 11).

4. Conclusions

The rate of hydrogen production by photocatalysis of water was high when photocatalysis was assisted by ultrasound. The ultrasound enhanced the rate of mass transfer of hydrogen from the surface of the catalyst to bulk. This enhancement was because of the fact that the mechanical energy of the ultrasound caused faster bubble detachment and thus making a larger fraction of catalyst-surface available for adsorption of reactants and surface reaction. As the concentration of hydrogen built up in the system, the hydrogen production rate dropped down in both cases, i.e., with and without ultrasound. The reaction was kinetically controlled by desorption of product hydrogen. As the concentration of hydrogen increased, the rate of desorption and consequently the rate of overall process became slow. When the electrolyte solution was purged off hydrogen, the activity was completely regained.

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