

Research Article

In Situ Measurement of Local Hydrogen Production Rate by Bubble-Evolved Recording

Xiaowei Hu, Liejin Guo, and Yechun Wang

State Key Laboratory of Multiphase Flow in Power Engineering, International Research Center for Renewable Energy, Xi'an Jiaotong University, Shaanxi 710049, China

Correspondence should be addressed to Xiaowei Hu; hu-xiaowei@mail.xjtu.edu.cn and Liejin Guo; lj-guo@mail.xjtu.edu.cn

Received 15 January 2013; Accepted 18 February 2013

Academic Editor: Krisztina Gajda-Schranz

Copyright © 2013 Xiaowei Hu et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Hydrogen visibly bubbles during photocatalytic water splitting under illumination with above-bandgap radiation, which provides a direct measurement of local gas-evolving reaction rate. In this paper, optical microscopy of superfield depth was used for recording the hydrogen bubble growth on $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ photocatalyst in reaction liquid and illuminated with purple light. By analyzing change of hydrogen bubble size as a function of time, we understood that hydrogen bubble growth experienced two periods, which were inertia effect dominated period and diffusion effect dominated period, respectively. The tendency of hydrogen bubble growth was similar to that of the gas bubble in boiling, while the difference in bubble diameter and growth time magnitude was great. Meanwhile, we obtained the local hydrogen production rate on photocatalyst active site by measuring hydrogen bubble growth variation characteristics. This method makes it possible to confirm local actual hydrogen evolution rate quantitatively during photocatalytic water splitting.

1. Introduction

Hydrogen production from solar energy by splitting water directly using semiconductor material is a promising source of carbon-free energy [1]. A lot of research has been developed on the performance improvement of semiconductor material by providing active sites and structuring semiconductor surface [2–7]. But for the heterogeneous photocatalytic reaction system, many issues concerning the semiconductor-liquid interface remain unsolved, such as the nature of the active sites and confirmation for actual reaction rate and hydrogen evolution rate [8, 9].

Hydrogen visibly bubbles during water splitting process, which couples the effects of the solid-liquid interface, hydrogen transfer process, and the multiphase system. Taking water splitting of photocatalysis, for example, due to the heterogeneous system, the reactant molecules will absorb on the catalyst surface before the photocatalytic reaction starts. When the lights radiate on the catalyst, hydrogen will start to evolve. The hydrogen generated will dissolve in the liquid adjacent to the catalyst surface firstly and will gather at solid-liquid interface randomly. When the gas gathering energy is

equal to or larger than the interface-free energy, bubble will start to nucleate and grow, and then, the local concentration and supersaturation degree are both critical values. Driven by the hydrogen molecules transfer due to supersaturation degree, finally hydrogen bubble will grow to a maxim size and detach from the catalyst surface into the reaction liquid. The hydrogen will be generated continuously, and hydrogen bubble will evolve on the same site continuously during the reaction process. The investigations on hydrogen bubble evolution characteristics will help understanding the hydrogen transfer process and the effects of the solid-liquid interface and heterogeneous system, but the research on this field is almost blank.

On the other hand, the hydrogen evolution rate or the reaction rate is a key parameter during hydrogen production process [10]. However, the determination for the hydrogen evolution rate precisely is believed to be difficult. Usually, during the process of photocatalytic water splitting, the hydrogen production rate is reflected by gas chromatograph. For the photoelectrochemical water splitting, the parameter of photocurrent is analyzed as a reaction rate index. The common approach mentioned above could not analyze the nature

TABLE I: Experimental conditions in this paper.

Reaction liquid	Photocatalyst	Incident light
Na_2SO_3 (0.25 mol/L)/ Na_2S (0.35 mol/L)	$\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ /mass fraction 1%	Purple light

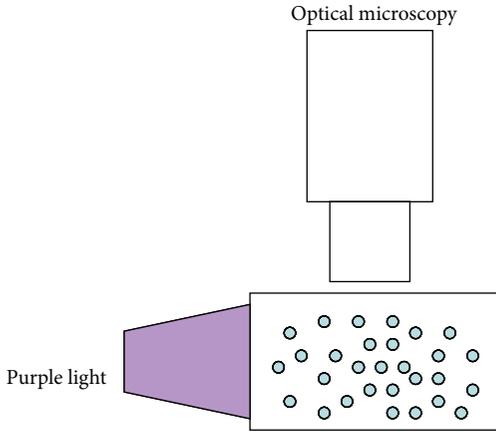


FIGURE 1: Reaction and measurement system.

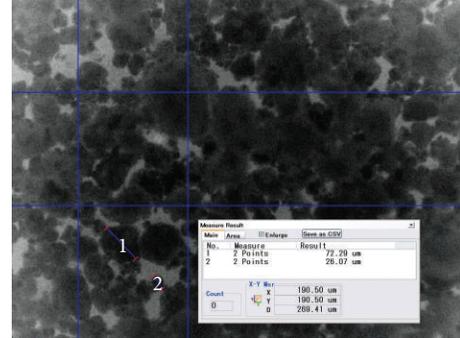
of the local active sites or the structuring surface providing only the average reaction rate. While methods based on local activity could offer a wealth of information about the surface sites important for efficient charge transfer. Examining the evolved hydrogen bubbles could provide a local measurement by recording growth rate. Additionally, measuring the bubble and the actual gas produced provides a more accurate value than that obtained by gas chromatograph or photocurrent. The straight technique of optical microscopy provides a localized measurement of the hydrogen production rate or reaction rate [9].

In this paper, the hydrogen bubble evolution process in photocatalytic reaction will be investigated. By the bubble growth recording, the research on bubble growth characteristics will be carried out, clearing the hydrogen transfer process and key affecting factors. Meanwhile, the hydrogen production rate on local active sites will be obtained and analyzed.

2. Experimental Section

In this paper, the whole experimental system was shown in Figure 1. Generally, photocatalyst, reaction liquid, and illumination conditions are the main factors affecting the reaction process. In this paper, the reaction system of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ photocatalyst which was prepared by precipitation-hydrothermal method with nanotwins [11] in reaction liquid of Na_2SO_3 (0.25 mol/L)/ Na_2S (0.35 mol/L) under the illumination of purple light was applied, as shown in Table I. On the other hand, temperature is also a key parameter during bubble evolving by affecting gas molecules movement and transfer process. Here, the operating temperature is 25°C.

Generally speaking, the high speed camera was used to record the bubble growth. But under the photocatalytic conditions, the size scale for hydrogen bubble is relatively

FIGURE 2: $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ photocatalyst in liquid.

small due to the heterogeneous system of photocatalyst. The resolution radius for ordinary high speed method will not meet the requirements. In order to catch the growth process well, a microscopy photography method by Keyence/VHX-600 was used in this paper, and the catalyst distribution in reaction liquid is shown in Figure 2.

3. Results and Discussion

3.1. Hydrogen Bubble Growth Characteristics. The hydrogen generated firstly dissolves in the reaction liquid and then nucleates to form bubble when the hydrogen concentration reaches supersaturation point. Interface between catalyst and reaction liquid lowers the free energy for bubble nucleation, which is a typical heterogeneous bubble nucleation process. In the process of photocatalysis, hydrogen bubble grows continuously and finally detaches from the solid-liquid interface reaching maximum diameter.

Research on bubble growth has been carried out systematically based on the nucleate boiling phenomena [12–15]. The bubble growth process has been divided into stages with inertia effects controlled and stages with diffusion effects controlled [16]. At the initial stage, the bubble growth is driven by the pressure difference between the outside and inside of the bubble interface for its large value according to the Laplace equation. Surface tension and other inertia effects will prevent the growth, called by inertia effects controlled stage with a high bubble growth rate. With the growth of the bubble, the pressure difference between the outside and inside of the bubble interface becomes smaller, and the transfer process of gas molecules from outside to inside becomes the key factor preventing bubble growth. So the later stage is called diffusion effects controlled stage. During this stage, the bubble growth rate is relatively small.

Figure 3 shows the hydrogen bubble growth characteristics during a bubble growth period and the comparison with the bubble growth under the condition of nucleate boiling

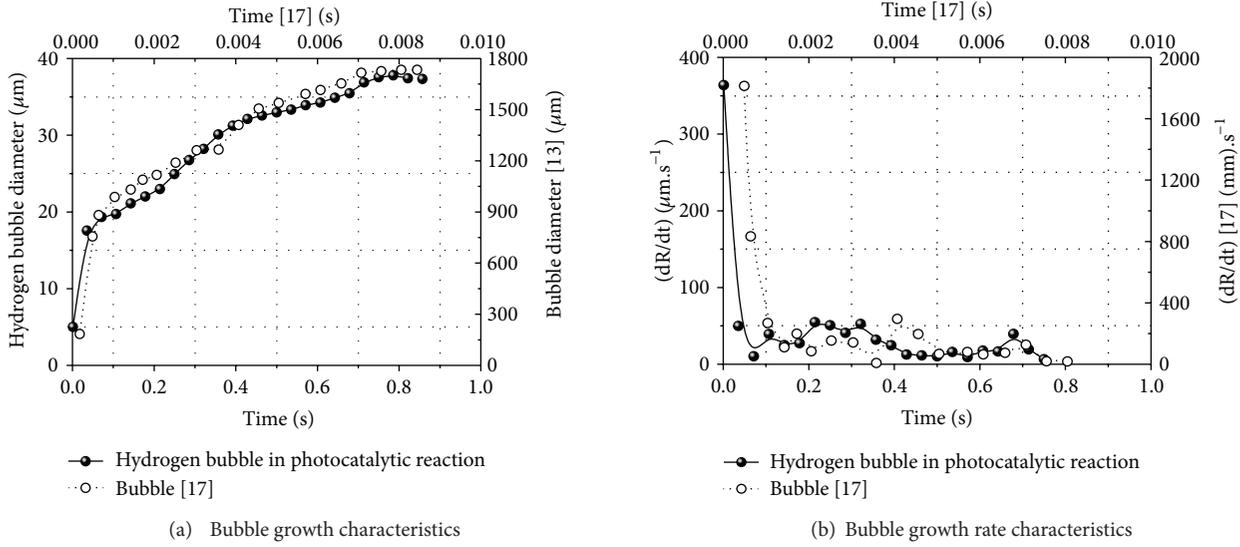


FIGURE 3: Hydrogen bubble growth characteristics during a bubble growth period and the comparison with the bubble growth under the condition of nucleate boiling.

in n-pentane liquid of $P = 760$ mmHg, $T_w - T_s = 31^\circ\text{F}$ in the literature [17]. From the figure, we can understand that the characteristics of hydrogen bubble in photocatalysis and bubble in nucleate boiling are almost consistent that the whole periods of bubble growth contain two stages with different growth rates. However, there are apparent differences between time scale and bubble size scale. Under photocatalysis condition, a whole growth period was about one second including hydrogen bubble from nucleation to detachment with max bubble diameter of 40 micrometers, while a whole growth period was about 100 milliseconds with max bubble diameter of 2 millimeters under the conditions of nucleate boiling. For the hydrogen bubble, hydrogen bubble grows rapidly to a certain size at the first stage of inertia effects controlled, and after that, the growth rapid slows down turning into the longer stage of hydrogen molecular diffusion effects controlled. Figure 4 shows a typical hydrogen bubble growth period on an active site of photocatalyst.

On the other hand, hydrogen bubble generates periodically as shown in Figure 5. After the first bubble evolution, hydrogen bubble will evolve continuously under the purple lights radiation. The period for bubble evolution can be described by nucleation time t_n and growth time t_g . Nucleation time describes the time from bubble detachment to nucleation of a new bubble, and growth time describes the time from the bubble nucleation to bubble detachment. The two parameters reflect the influences of growth process and nucleation process on the whole bubble evolution period. Generally, if $t_g/t_n > 1$, the influence of growth process is more important, which means that the effects of gas molecules transfer process are the key factors. On the contrary, the influence of nucleation process is more important, which means that the effects of supersaturation degree or reaction rate are dominated. Figure 5 indicates that the nucleation time is larger than growth time during the whole bubble

evolution period. That means that the photocatalytic reaction process driving bubble nucleation is the key factor affecting the hydrogen mass transfer process during hydrogen evolution.

3.2. Hydrogen Production Rates. Assuming for each bubble (i) an approximately spherical shape, (ii) a composition of gaseous hydrogen molecules, and (iii) a temperature equalling to the environment, according to the Laplace equation

$$P_i - P_o = \frac{2\gamma_{gl}}{R}, \quad (1)$$

and considering

$$P_i = P_{H_2}, \quad (2)$$

the number of hydrogen molecules inside the bubble can be calculated by ideal gas law

$$N_{H_2, \text{bubble}} = \frac{P_o + 2\gamma_{gl}/R}{kT} \frac{4}{3}\pi R^3, \quad (3)$$

where $P_o = 1.013 \times 10^5$ Pa is the ambient pressure, γ_{gl} is the gas-liquid surface tension, k is Boltzmann's constant, and $T = 298$ K is the ambient temperature. So we can obtain the variation of hydrogen gas in bubble with time, as shown in Figure 6.

In fact, the hydrogen produced exists in two parts: gas in bubble and gas dissolving in liquid. When the bubble starts to form, the concentration of hydrogen in liquid is supposed to reach the saturation value, achieving stable state. So, the variation of gas in bubble reflects the reaction production rate. Figure 7 shows the calculated local hydrogen production rate on an active site of photocatalyst. During the process of bubble evolution, the reaction rate was not stable, with a little

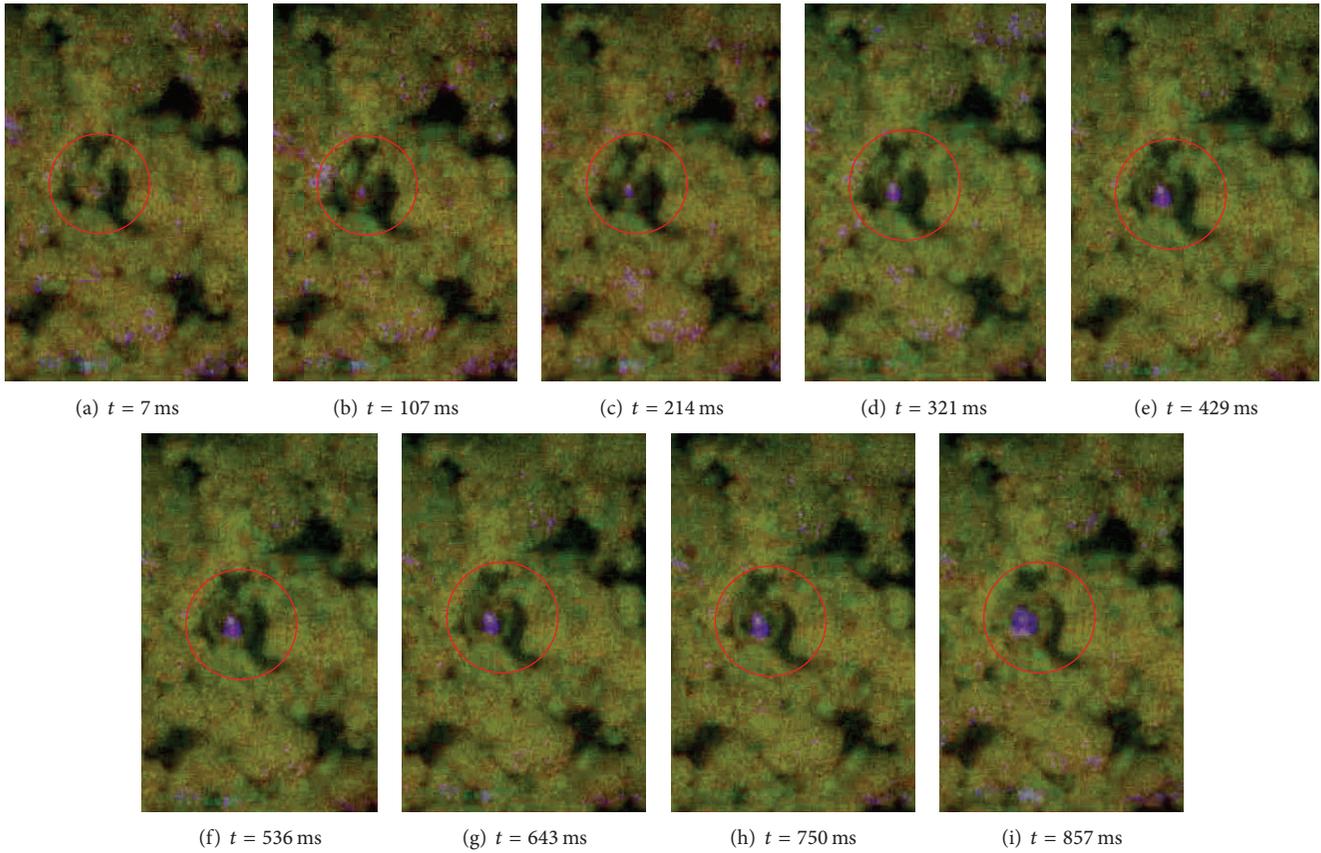


FIGURE 4: Hydrogen bubble evolution process.

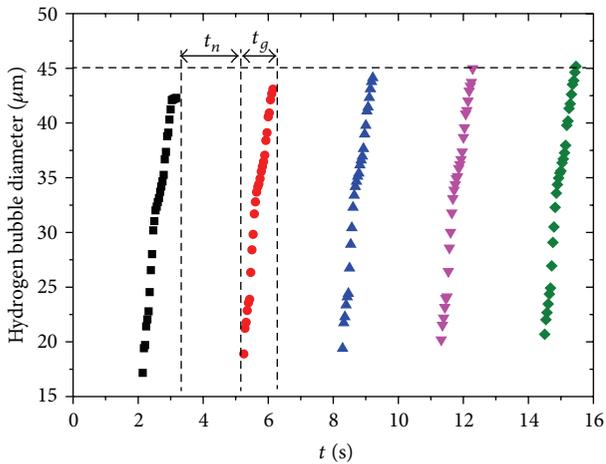


FIGURE 5: Hydrogen bubble evolution cycle on the selected site.

fluctuation, which is mostly caused by the “bubble-shadow effect.” The bubble will scatter some lights during evolution, affecting the local photon energy absorption of photocatalyst and influencing the active site performance.

Recording bubble growth during photocatalysis provides a way for local hydrogen production rate determination on a certain site. Unlike the average hydrogen production rate

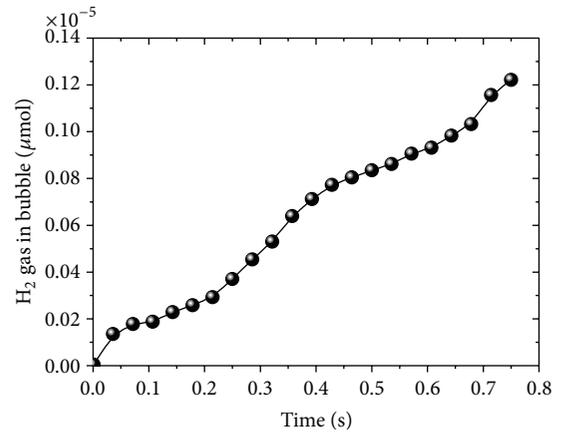


FIGURE 6: Calculated hydrogen evolution rate from gas bubble.

over some time, this local hydrogen production rate contains wealth of information about the active site and can help for understanding of the catalyst surface characteristics and its photocatalytic performance directly.

4. Conclusions

In this study, by above-bandgap light illuminating on $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ photocatalyst, evolving of individual hydrogen

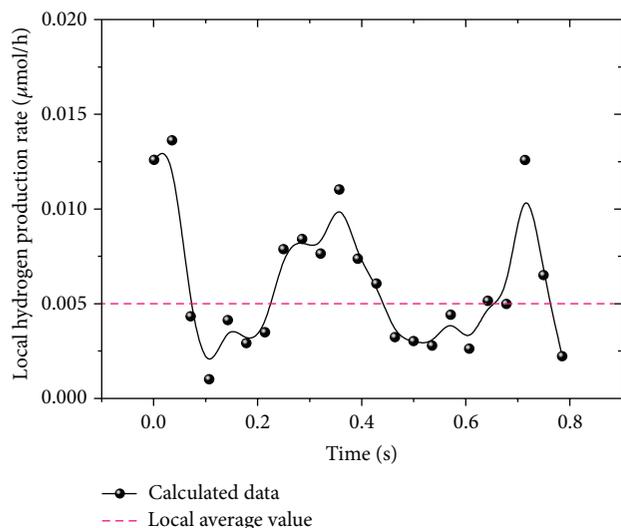


FIGURE 7: Calculated local hydrogen production rate (red dashed line indicates the average value in a bubble evolution period).

bubble, and recording of the hydrogen bubble growth, we analyzed the hydrogen bubble growth characteristics. Hydrogen bubble growth experienced two periods, which are inertia effect dominated period and diffusion effect dominated period, respectively. The tendency of hydrogen bubble growth is similar to that of the gas bubble in boiling, while the difference in bubble diameter and growth time magnitude is great. We also found that the nucleation time of hydrogen bubble was larger than the growth time, which means that the nucleation process is the key factor during the whole process of hydrogen bubble evolution.

We also provide an in situ direct and quantitative measurement of local hydrogen production rate. The variation of local hydrogen production rate indicates the effects of bubble shadow on local photon energy absorption of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ photocatalyst. The results also provide the possibility of comparing the effects of different heterogeneous catalyst or morphology on photocatalytic performance systematically.

Abbreviations

P_i :	The pressure of inside the bubble, Pa
P_{H_2} :	The pressure of hydrogen inside the bubble, Pa
P_o :	Ambient pressure, Pa
γ_{gl} :	Gas-liquid surface tension, $\text{N} \cdot \text{m}^{-1}$
R :	Bubble radius, m
$N_{\text{H}_2, \text{bubble}}$:	The number of hydrogen molecules inside the bubble
T :	Ambient temperature, K
k :	Boltzmann's constant, $1.038065 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$
t_n :	Nucleation time, s
t_g :	Growth time, s.

Conflict of Interests

The authors declare no conflict of interest.

Acknowledgments

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (no. 51236007, no. 51121092, and no. 51102194) National Basic Research Program of China (no. 2009CB220000). One of the authors (X. Hu) was supported by the "Fundamental Research Funds for the Central Universities."

References

- [1] J. Nowotny, C. C. Sorrell, L. R. Sheppard, and T. Bak, "Solar-hydrogen: environmentally safe fuel for the future," *International Journal of Hydrogen Energy*, vol. 30, no. 5, pp. 521–544, 2005.
- [2] Z. G. Zou, J. H. Ye, K. Sayama, and H. Arakawa, "Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst," *Nature*, vol. 414, no. 6864, pp. 625–627, 2001.
- [3] S. U. M. Khan, M. Al-Shahry, and W. B. Ingler, "Efficient photochemical water splitting by a chemically modified n-TiO_2 ," *Science*, vol. 297, no. 5590, pp. 2243–2245, 2002.
- [4] A. Kudo and Y. Miseki, "Heterogeneous photocatalyst materials for water splitting," *Chemical Society Reviews*, vol. 38, no. 1, pp. 253–278, 2009.
- [5] K. Maeda and K. Domen, "Photocatalytic water splitting: recent progress and future challenges," *The Journal of Physical Chemistry Letters*, vol. 1, no. 18, pp. 2655–2661, 2010.
- [6] J. S. Lee, "Photocatalytic water splitting under visible light with particulate semiconductor catalysts," *Catalysis Surveys from Asia*, vol. 9, no. 4, pp. 217–227, 2005.
- [7] X. B. Chen, S. H. Shen, L. J. Guo, and S. S. Mao, "Semiconductor-based photocatalytic hydrogen generation," *Chemical Reviews*, vol. 110, no. 11, pp. 6503–6570, 2010.
- [8] M. W. Kanan and D. G. Nocera, "In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co^{2+} ," *Science*, vol. 321, no. 5892, pp. 1072–1075, 2008.
- [9] A. J. Leenheer and H. A. Atwater, "Water-splitting photoelectrolysis reaction rate via microscopic imaging of evolved oxygen bubbles," *Journal of the Electrochemical Society*, vol. 157, no. 9, pp. B1290–B1294, 2010.
- [10] M. Ni, M. K. H. Leung, D. Y. C. Leung, and K. Sumathy, "A review and recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production," *Renewable and Sustainable Energy Reviews*, vol. 11, no. 3, pp. 401–425, 2007.
- [11] M. C. Liu, L. Z. Wang, M. Lu, X. D. Yao, and L. J. Guo, "Twins in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ solid solution: highly efficient photocatalyst for hydrogen generation from water," *Energy and Environmental Science*, vol. 4, no. 4, pp. 1372–1378, 2011.
- [12] M. S. Plesset and S. A. Zwick, "The growth of vapor bubbles in superheated liquids," *Journal of Applied Physics*, vol. 25, no. 4, pp. 493–500, 1954.
- [13] H. K. Forster and N. Zuber, "Growth of a vapor bubble in a superheated liquid," *Journal of Applied Physics*, vol. 25, no. 4, pp. 474–478, 1954.
- [14] G. Son, V. K. Dhir, and N. Ramanujapu, "Dynamics and heat transfer associated with a single bubble during nucleate boiling

- on a horizontal surface,” *Journal of Heat Transfer*, vol. 121, no. 3, pp. 623–631, 1999.
- [15] A. Asai, “Bubble dynamics in boiling under high heat-flux pulse heating,” *Journal of Heat Transfer*, vol. 113, no. 4, pp. 973–979.
- [16] A. J. Robinson and R. L. Judd, “The dynamics of spherical bubble growth,” *International Journal of Heat and Mass Transfer*, vol. 47, no. 23, pp. 5101–5113, 2004.
- [17] R. Cole and H. L. Shulman, “Bubble growth rates at high Jakob numbers,” *International Journal of Heat and Mass Transfer*, vol. 9, no. 12, pp. 1377–1390, 1966.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

