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Preparation of Quantized Zinc Sulfide Particles and their Photocatalytic Hydrogen Evolution in Aqueous Methanol Solution

量子化ZnS纳米颗粒的制备及其在甲醇水溶液中光催化产氢

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Based on our previous studies, in which 1-nm ZnS particles were obtained by embedding them in β -cyclodextrin cavities (denoted as ZnS/BCD), this work focused on the photocatalysis of these extremely small ZnS particles in hydrogen evolution and selective production of ethylene glycol from aqueous methanol solution under illumination with either low- or high-pressure mercury lamp. The ZnS/BCD inclusion complex was distinctly more active than the best colloidal ZnS system we ever developed, while a physical mixture of ZnS and BCD did not improve the activity. The quantum yield of hydrogen evolution was 0.71 for the ZnS/BCD and 0.31 for the mixture. This indicates that quantum size effects exist and operate in the photocatalysis.

INTRODUCTION

The zinc sulfide photocatalytic system has been shown to be capable of highly selective production of organic compounds as well as efficient hydrogen evolution [1-3]. According to Yanagida [1], ZnS is a semiconductor of larger band gap (3.66 eV), the reducing power of which, as a result of photoexcitation, is strong enough to enable hydrogen to be evolved from water without any modification of noble metal and the photogenerated holes, a positive charge center left in the valence band of which, can oxidize various organic substrates and thus be synthetically significant. Our recent publications [3] showed that highly efficient photocatalytic production of hydrogen and ethylene glycol from aqueous methanol solution can be achieved in the presence of fresh colloidal ZnS under UV irradiation.

On the other hand, research on the photocatalysis of extremely small semiconductor particles with quantum size effects [4] (often known as Q-particles) is becoming an active and competitive field [5-9]. In the context of photocatalysis, the quantum size effects, arising from the confinement of photogenerated charge carriers in nanometer semiconductors with potential wells of small dimensions and being recognizable by a blue-shifting exciton peak in the absorption spectrum, are expected in the following ways: (a) increase of active reaction center due to larger surface to bulk

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ratio; (b) increase of redoxing potential due to higher energy band level shifts; (c) increase of reaction probability due to faster arrival of the photoinduced electron and hole to reaction center on surface instead of recombination, hence higher quantum yield may be expected. However, problems have been encountered in the attempt to realize expectations such as how to make macroscopic amounts of stabilized and characterized Q-particles. One not only needs to achieve significantly more narrow size distribution but also to have precise control over the surface chemistry of these Q-particles. Especially in the case of photocatalysis, other more important factors should be fully taken into consideration, e.g., how to fabricate channels which are available for transmission of photons, electrons and holes, reactants and products. Efforts have been made in these respects. Among them, studies on the host/guest association of Q-particles with clays [7-8] are interesting and enlightening in that it provides a nanoscale lithographic tool to "ship in bottle" these Q-particles with well-defined structure and is thus a good basis for further researches. In the literature, Yoneyama *et al.* reported that 15-Å TiO_2 in clay was more active than TiO_2 powder in the photocatalysis of decomposition of 2-propanol, the quantum yield of which was 0.045% and 0.0028% respectively for TiO_2/clay and TiO_2 powder, 23.5% and 1.98% respectively for $\text{Pt-TiO}_2/\text{clay}$ and Pt-TiO_2 powder [7]. In contrast, Enea *et al.* reported that the efficiency of the best $\text{ZnS/CdS}/\text{clay}$ catalyst for hydrogen evolution in a S^{2-} medium was about four times lower than that for a SiO_2 -supported system under similar conditions [8].

Recently, we reported that 1-nm ZnS Q-particles can be, in the form of inclusion complex, obtained by embedding them in β -cyclodextrin (BCD) cavity [10]. The inclusion complex ZnS/BCD was found to be soluble moderately in water and excellently in several organic solvents like DMSO; moreover, it was found to be readily obtained in powder. These results have led us to further investigate their photocatalytic behavior that may exhibit quantum size effects in hydrogen evolution and selective production of ethylene glycol from aqueous methanol solution.

EXPERIMENTAL

Preparation of ZnS/BCD catalyst

Preparation and characterization of the ZnS/BCD inclusion complex have been reported previously [10]. The preparation procedure, involving a rapid precipitation technique and a subsequent temperature treatment, was proved to be good for the formation of the BCD-included zinc sulfide Q-particles. The final solution was translucent and essentially transparent when diluted to about 10^{-4} M.

For the sake of industrialization, however, we suggest that a common operation be used. Our latest experimental results show that another simple procedure may also be conveniently adapted, though it results in only ca. 80 wt% ZnS/BCD inclusion complex [11]. This procedure is as follows. Saturated Na_2S solution was added dropwise to a vigorously stirred and N_2 -bubbled solution, which contained 10^{-2} M ZnSO_4 with BCD (SIGMA Chem. Co.), until pH 8.3. Then the resulting slurry

under N_2 atmosphere, peptized by a further temperature treatment (e.g., changing solution temperature first from 30 to 60 °C and then back to 30 °C, maintaining each of the three temperatures for two hours). The resulting solution was allowed to stand for later use.

The ZnS/BCD obtained was found to show no significant difference in optical absorption, emission or XRD pattern from the one obtained using the procedure described in Ref.10. The amount of ZnS in the supernatant of ZnS/BCD solution at 3 °C, as determined by elemental analysis, was 13.78 mM.

Besides the ZnS/BCD, colloidal ZnS catalysts (ZnS-1 by the temperature treatment; ZnS-3 without undergoing the treatment) and a physical mixture (ZnS-2) of ZnS-1 and BCD were prepared under comparable preparation conditions as the reference.

Photocatalytic experiments

The experiments were carried out in an inner irradiation quartz reactor with magnetic stirring. The reactor was completely immersed in a constant temperature bath at 35 °C. 120-ml reaction solution ($CH_3OH / H_2O = 3 / 1$ v/v, 8.3×10^{-3} M ZnS/BCD, pH~10) was deaerated by bubbling N_2 for 15 min before illumination. A 125-W high-pressure Hg lamp (purchased from Dalian Mercury Lamp Plant) or a 9-W low-pressure Hg lamp (>95% of the irradiation intensity in 2537 Å wavelength, purchased from Beijing Institute of Electronic Light Sources) was employed.

Products were analyzed by gas chromatography: hydrogen with the use of molecular sieve 5 Å (TCD detector) and ethylene glycol with Parapak Q (FID detector), respectively.

Irradiation intensity of a low-pressure Hg lamp used was, measured by ferrioxalate actinometry, 3.596×10^{-6} einstein $\cdot s^{-1}$. The maximum deviation of the data obtained was within $\pm 3\%$. The quantum yield for photocatalytic production of hydrogen was determined by assuming that two photons produce one molecule of H_2 .

RESULTS AND DISCUSSION

Blank tests.

The results of the blank tests are shown in Table 1. It can be seen from the table that: (a) in the absence of ZnS, no hydrogen evolution was observed (nos. 1~4), though only a trace of it was detected in the cases of strong alkaline and strong UV irradiation for a long time [3]. These results indicated that hydrogen was principally produced by photocatalysis of ZnS; (b) the ZnS/BCD was stable in water even if the solution was subjected to centrifugal treatment (4000 r.p.m., 30 min.), whereas the colloidal ZnS was not and must be greatly removed from the solution (nos. 5~6); (c) cooling treatment of catalyst solution may cause a decrease in solubility, and therefore, a decrease in photocatalytic production. However, the cooling effect on hydrogen production did not equally affect the ZnS/BCD solution or colloidal ZnS solution (nos. 7~8). The results (nos. 4~8) suggested that they were chemically and physically different; (d) blank tests confirmed that BCD molecule

exhibited itself to be a weak electronic donor and participated in the photocatalytic redox process when CH_3OH was absent (no. 9). Hence, it is likely that BCD acts as an "electronic relay", which transfers hole and electron between the reactants and the included ZnS particles.

Table 1. Blank tests for hydrogen evolution

test no.	catalysts	BCD* (ml)	CH_3OH (ml)	initial pH	H_2 (ml)	irradiation time (hr)
1	(absent)	0	0	11.45	0	2 (2)
2	(absent)	0	90	11.56	0	2 (2)
3	(absent)	90	0	11.45	0	2 (2)
4	(absent)	30	90	11.50	0	3 (2)
5	coll. ZnS (a)	0	50	10.36	0	4 (1)
6	ZnS/BCD (a)	0	50	10.84	79	4 (1)
7	coll. ZnS (b)	0	50	10.05	6	4 (2)
8	ZnS/BCD (b)	0	50	9.33	45	3 (2)
9	ZnS/BCD (b)	0	0	10.33	89	4 (2)

BCD*: saturated solution was used. (1) or (2): refers to high- or low-pressure mercury lamp, (a) or (b): to the supernatant of centrifugal or cooling treatment.

Hydrogen evolution experiments

Fig 1(a) and (b) demonstrate the hydrogen evolution catalyzed by different kinds of ZnS under irradiation of high-pressure Hg lamp and low-pressure Hg lamp. For the convenience of description, we define R as the ratio of hydrogen production rates

(data are acquired from linear fit equation) for the ZnS/BCD to other reference catalysts. So R_1 refers to the ratio of ZnS/BCD to ZnS-1, R_2 to ZnS-2 and R_3 to ZnS-3, respectively. They are listed in Table 2.

By comparing these Rs, we realized that R, ranging from 1.28 to 2.40, is always larger than unity. These experimental results confirmed that the extremely small ZnS particles included in BCD cavities were more photocatalytically active than those ZnS catalysts of larger particle size, including the most active colloidal ZnS catalyst we ever developed [3]. The overall quantum yield determined was 0.71, 0.54, 0.31 and 0.26 respectively for ZnS/BCD, ZnS-1, ZnS-2 and ZnS-3. In another feature, R_2 is larger than R_1 , especially in the case of low-pressure Hg lamp, i.e., the sequence of the working efficiency is ZnS-1 > ZnS-1 + BCD mixture. This indicated that in the case of non-inclusion between ZnS and BCD, an inhibition to the photocatalytic activity of ZnS would occur because of mass transfer and accessibility problems in such a BCD-convoluted system. Accordingly,

Table 2. Ratios of hydrogen production rates (R values)

Hg lamp	R_1	R_2	R_3
h.p.	1.28	1.37	1.93
l.p.	1.31	1.88	2.40

the high efficiency between ZnS and BCD, thus the quantum yield loss caused by the high-pressure lamp. The hydrogen production rate measured by spectrometric method is around 245 $\mu\text{mol/h}$, compared to 100 $\mu\text{mol/h}$ between the blank and ZnS. This suggests that the addition of BCD markedly improves the hydrogen production rate, as discussed on

Hydrogen production (ml)

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200

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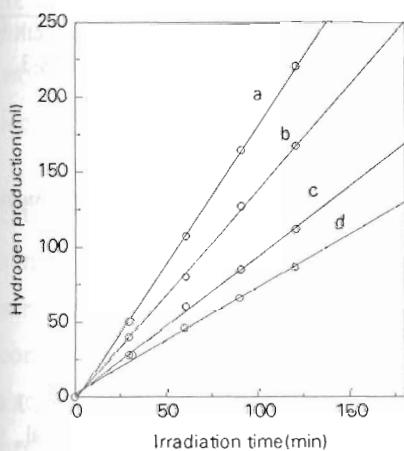
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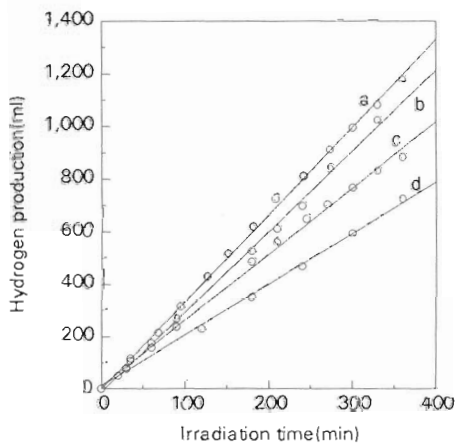
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redox process relay", which the high efficiency of the ZnS/BCD catalyst for H₂ evolution must greatly contribute to the inclusion between ZnS semiconductors and BCDs, which brings about the formation of ZnS Q-particles and thus the quantum size effects. Clearly, it is the quantum size effects that largely compensate for the loss caused by the inhibition mentioned above. We can also find that the value of R in the low-pressure lamp is always larger than that in the high-pressure lamp. In other words, the relative rate of hydrogen production is higher in the low-pressure lamp and lower in the high-pressure lamp. The spectrometric evidence [10] showed that a sharp exciton peak appeared in the absorption band around 245 ~ 250 nm (5.0 ~ 5.1 eV) for the ZnS/BCD inclusion complex, a heavy blue shifting compared to the absorption edge for colloidal ZnS. So, a better match in energy should exist between the band gap of the included ZnS and the excitation from the low-pressure lamp. This again suggests that the ZnS particles in the ZnS/BCD are extremely small and exhibit quantum size effects. Moreover, R₃ was found to be larger than R₁. This means that the temperature treatment also affects markedly the photocatalytic activity of H₂ production for colloidal ZnS. This subject will be discussed on other papers under preparation.



(a)



(b)

Fig. 1. Photocatalytic hydrogen production as a function of illumination time with low-pressure Hg lamp (Fig. 1(a)) and high-pressure Hg lamp (Fig. 1(b)). Curves labeled a, b, c and d represent the hydrogen evolution catalyzed by ZnS/BCD, ZnS-1, ZnS-2 and ZnS-3, respectively.

It continues to be a problem whether or not the higher activity of the ZnS/BCD comes mainly from its higher surface area, since the direct measurement of the effective surface area seems to be difficult. It is noteworthy, however, that Inoue et al. reported that the size quantization of ZnS on SiO₂ enhanced the photocatalytic activity of CO₂ reduction, the degree being roughly independent on the surface area [9]. The finding would be theoretically valuable to a more explicit explanation of our results if such a relationship really exists.

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Selective production of ethylene glycol

The selectivity of ethylene glycol (EG), moles of EG/moles of H₂ (%), is listed in Table 3. The data shown in the table indicate that the colloidal ZnS exhibited moderate selectivity, roughly independent of what kind of Hg lamp was used, whereas the ZnS/BCD and the ZnS + BCD mixture did not. In a general way, the BCD-presented catalysts appeared to be more favorable to selectively produce EG from aqueous methanol solution. It was believed that quantum size effect would make the valence band potential more positive, in which the hole would oxidize compounds with less chemical discrimination, so the EG selectivity in the case of ZnS/BCD would decrease. To say the least, the quantum size effect should not benefit selective EG production. A possible explanation to the better results of EG selectivity in the case of BCD-presented catalysts would be in that the excess free BCD molecules introduced in the preparation, may accommodate the photocatalytically-generated $\cdot\text{CH}_2\text{OH}$ radicals by forming $\cdot\text{CH}_2\text{OH}/\text{BCD}$ inclusion complexes, and protect the radicals from being deep photo-oxidation, and thereafter, promote the coupling reaction between them.

Table 3. Selectivity of ethylene glycol(%)

Hg lamp	ZnS/BCD	ZnS-1*	ZnS-2
h.p.(4 hr)	69.4	41.5	94.4
l.p.(2 hr)	96.0	42.7	51.5

* Only a slight difference in selectivity had been found between ZnS-1 and ZnS-3.

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- A certain amount of larger ZnS aggregates were observed at the bottom of the solution. ZnS/BCD particles can dissolve excellently in DMSO, while these aggregates can not, so the amount was roughly determined.