

PHOTOCATALYSIS OF ZINC SULFIDE MICROCRYSTALS  
IN REDUCTIVE HYDROGEN EVOLUTION IN WATER/METHANOL SYSTEMSShozo YANAGIDA,\* Hiroshi KAWAKAMI, Kazuhito HASHIMOTO,<sup>†</sup>  
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In photocatalytic H<sub>2</sub> evolution using an aq. methanol system, high quality microcrystalline (cubic) ZnS powders have been found to be active under an appropriate light intensity, which is comparable in activity with freshly prepared ZnS suspensions. Comparison of photoactivities of some commercial ZnS with their surface properties has revealed that the surface purity of ZnS plays an important role in the photocatalysis, while the luminescence observed at 445 nm for the high quality ZnS microcrystals was not affected in the presence of oxygen, diethylamine, or methylviologen.

Previously we reported that ZnS suspensions prepared *in situ* from aq. ZnSO<sub>4</sub> and Na<sub>2</sub>S are very efficient as unmodified photocatalysts for UV light ( $\lambda > 290$  nm) photoredox reactions in aq. electron donor solutions; water is effectively reduced to evolve H<sub>2</sub> and some organic electron donors concurrently undergo one electron oxidation, leading to carbon-carbon bond formation via radical coupling reactions.<sup>1,2)</sup> However, commercial ZnS powders for electroluminescence (Mitsuwa EL grade) showed little activity compared with the freshly prepared ZnS suspensions, and the colloidal parts of the freshly prepared ZnS seemed to play a decisive role in the photocatalysis. In fact, the acceleration of photochemical reactions by colloidal particles received much attention.<sup>3-6)</sup> On the other hand, the reported value for the conduction band edge of ZnS, -1.74 V vs. SCE (pH 1),<sup>7)</sup> suggests a strong reductive power of electron in the conduction band and also rationalizes the highly efficient H<sub>2</sub> evolution in the unmodified ZnS photocatalysis.

We now report that the high quality ZnS microcrystal dispersions are as active in photoreductive H<sub>2</sub> evolution as the freshly prepared ZnS suspensions.

In order to evaluate the photoelectron transfer activity of some commercial ZnS, the photoreductive H<sub>2</sub> evolution was investigated using an N<sub>2</sub> purged aq. methanol system. The physical properties of the examined ZnS, the reaction conditions, and the quantum yields measured on 313 nm irradiation are summarized in Table 1.

Compared with the quantum yield, 0.14, for the freshly prepared ZnS,<sup>2)</sup> the commercially available CP grade ZnS powders have been found to have fairly good activities. Surprisingly, Nakarai GR grade ZnS crystals, which have the smallest surface area of the examined ZnS, show the highest activity. It should be noted that, under highly intense light like an internal UV irradiation, Nakarai ZnS powders blacken due to the photoformed metal Zn and gradually lose the activity. As we reported previously, Mitsuwa EL grade ZnS powders were confirmed to be ineffective in their activity without the blackening.

Observation by scanning electron microscopy reveals that Shimakyu ZnS powders are fine particles (Fig. 1a), Nakarai ZnS powders consist of crystalline

Table 1. The Physical Properties and the Photocatalytic Activity of Some Commercial ZnS Powders

ZnS	Purity %	Particle size $\mu\text{m}$	Surface <sup>a)</sup> area/ $\text{m}^2\text{g}^{-1}$	Crystal form <sup>b)</sup>	Reaction conditions <sup>c)</sup> ZnS/ $\mu\text{mol}$	Quantum yield <sup>d)</sup> $\Phi(1/2\text{H}_2)$ (react. time/h) <sup>e)</sup>
Shimakyu (CP grade)	f)	<0.1 <sup>g)</sup>	14.4	c	104	0.055(5), 0.057(6)
Wako (CP grade)	-	<0.1 <sup>g)</sup>	7.0	c/h	150	0.017(5), 0.023(10)
Nakarai (GR grade)	99.99	av. 3	<1	c	108	0.093(5), 0.092(21)
Mitsuwa (EL grade)	h)	av. 2	43.2	c	125	0.003(10)

a) Determined by BET method. b) h, hexagonal; c, cubic. c) Methanol(3 ml) and water(1 ml) were used. d) Determined using a 2-hexanone actinometer by assuming that two photons produce one molecule of  $\text{H}_2$  and corrected for light absorption by the suspended catalyst. e) Reactions were mostly carried out twice using the same reaction mixture. f) Contaminated with unknown crystalline salts, as determined by the X-ray diffraction pattern. g) Estimated by the scanning electron microscopy. h) Metallic impurity max. 5 ppm.<sup>8)</sup>

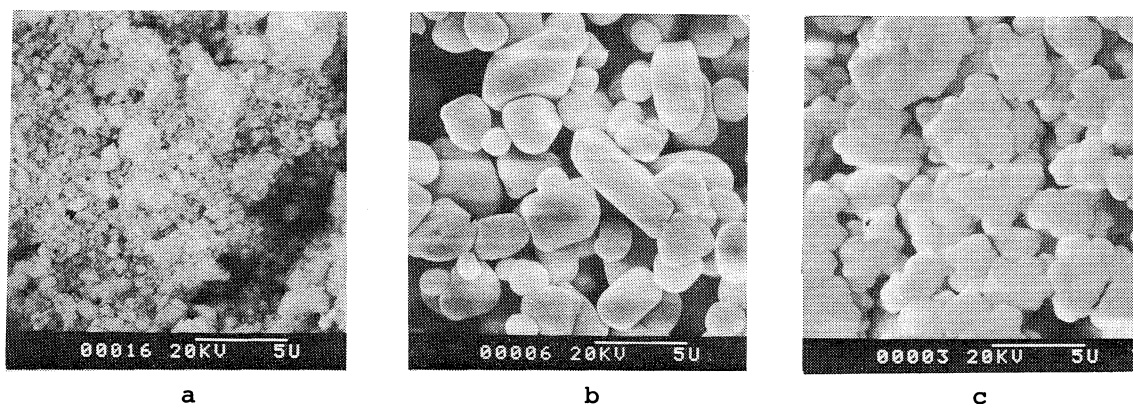


Fig. 1. Scanning electron micrographs of commercial zinc sulfide powders. a: Shimakyu CP Grade, b: Nakarai GR Grade, c: Mitsuwa EL Grade.

particles (Fig. 1b), and Mitsuwa ZnS powders are porous particles, i.e., have the structure of second order particles composed of smaller particles (Fig. 1c). The porous structure explains the large surface area contrary to the apparent large particle size. These facts clearly indicate that the surface area is not necessarily an important factor affecting the photocatalytic activity.

Based on X-ray diffraction analysis, Nakarai ZnS powders were characterized to be cubic (sphalerite), both Mitsuwa and Shimakyu ZnS to be cubic contaminated by a small amount of hexagonal (wurtzite) form, and Wako ZnS to be a mixture of cubic and hexagonal forms. It is worth noting that Mitsuwa ZnS showed broad X-ray diffraction patterns.

The surfaces of Nakarai and Mitsuwa ZnS powders were investigated by ESCA. No substantial difference was observed in the spectra, indicating that the surface within a few nm are not different in composition. It should be mentioned that both ZnS powders were covered with oxygen atoms which were not removed even after heating at 400 °C for a period of 1 h followed by 0.5 h argon etching. This is probably due to the adsorbed O<sub>2</sub> which may diffuse into ZnS and/or the presence of oxidized ZnS species like ZnO on the surfaces.

The oxidative formation of ZnO on ZnS is supported by the photoacoustic spectra. As shown in Fig. 2, ZnO powders show a sharp onset at 400 nm, and the most effective ZnS powders obtained by evaporating to dryness the *in situ* prepared ZnS suspension (which involved Na<sub>2</sub>SO<sub>4</sub>) showing a sharp onset at 370 nm. The less active Wako ZnS have an onset at around 400 nm, indicating contamination by ZnO. The inactive Mitsuwa ZnS shows the spectrum which "tails" from 400 nm to 480 nm, indicating the presence of ZnO on the surface and/or the presence of surface defects attributable to metallic impurities (max 5 ppm).<sup>8)</sup> Since the photo-generated electron-hole pairs should be trapped by such oxide surface or impurity levels and then inactivated, Mitsuwa ZnS was concluded to show little activity in the photocatalytic reaction.

Recently, Henglein and Gutierrez reported the photoluminescence of the colloidal ZnS and its quenching by electron donors and acceptors.<sup>9)</sup> Since the most active Nakarai ZnS was found to show the strongest photoluminescence with a maximum at 445 nm under air at room temperature, the relationship of the luminescence with photoelectron transfer reactions was examined.

The decay of the luminescence shown in Fig. 3 was different in lifetime ( $\tau$ ) from that reported for the colloidal ZnS.<sup>9)</sup> The photoluminescence can be divided roughly into two components, fast ( $\tau_{\text{fast}} = 32$  ns) and slow ( $\tau_{\text{slow}} = 610$  ns) ones, whose spectra are different from each

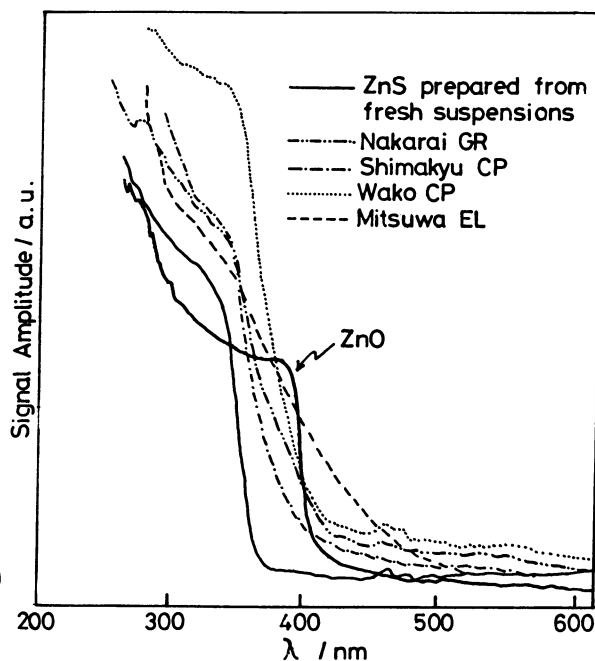


Fig. 2. Photoacoustic spectra of commercial ZnS powders.

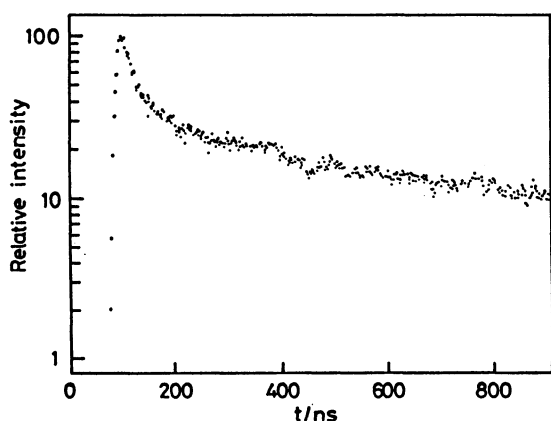


Fig. 3. Decay of Nakarai ZnS. Luminescence at 452 nm (under air at room temp). Light source: Pulsed N<sub>2</sub> laser, 6 ns, 337 nm.

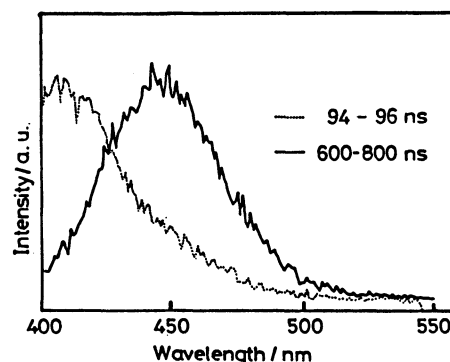


Fig. 4. Time-resolved luminescence spectra of Nakarai ZnS powder (under vacuum) observed with ns photon counting system.<sup>11)</sup> Light source: Pulsed N<sub>2</sub> laser, 6 ns, 337 nm.

other as shown in Fig. 4. However, the decay of the luminescence was not affected by further desorption of air by heating *in vacuo* to 300 °C and by the introduction of air. Further, neither diethylamine nor methylviologen quenched the luminescence emitted on 337 nm excitation in water. These facts are inconsistent with a recent report on the colloidal ZnS system.<sup>9)</sup> Since diethylamine is a good electron donor in the photocatalysis of ZnS,<sup>10)</sup> the electron-hole pairs which give rise to photoluminescence should be indifferent to interfacial reactions. Another source of electron-hole pairs should play an important role in electron transfer reactions.

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