



Predicting and identifying reactive oxygen species and electrons for photocatalytic metal sulfide micro–nano structures



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ABSTRACT

A broadly applicable theoretical and experimental framework was developed for understanding the photocatalytic mechanism of semiconductors. Using this framework, we found that it is possible to predict the type and reactivity of reactive oxygen species and electrons produced during photoexcitation of semiconductors by comparing the band edge energies of semiconductors with the redox potentials of relevant species. In addition, we could experimentally verify these predictions using electron spin resonance spectroscopy (ESR) with spin trapping and spin labeling techniques. We selected four types of metal sulfides (CdS, ZnS, In₂S₃, and Bi₂S₃) to elucidate the applicability of this model system. Using ESR technique, we found that these four sulfides are significantly different in the types of produced reactive oxygen species. When irradiated, ZnS can generate superoxide (O₂^{•-}), hydroxyl radicals (•OH), and singlet oxygen (¹O₂); CdS and In₂S₃ can produce O₂^{•-}, while irradiation of Bi₂S₃ generates none of these reactive oxygen species. These results are correlated with the photocatalytic oxidation and reduction activities of metal sulfide structures.

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1. Introduction

The increasing importance of semiconductor photoactivity in environmental remediation, energy conversion, and health care has stimulated a great deal of interest in understanding the fundamental photophysical and photochemical mechanisms underlying these applications [1]. The increasing of use of semiconductor nanomaterials has also led to new environment, health, and safety concerns [2,3]. Addressing these safety concerns also requires a better understanding of the mechanisms underlying the photoactivity of semiconductors. Light-driven generation of charge carriers (holes/electrons) and electron transfer are the initial crucial steps that determine the interaction between semiconductors and surrounding substances. The products of electron transfer, reactive oxygen species, including hydroxyl radical (•OH), superoxide (O₂^{•-}), and singlet oxygen (¹O₂), can lead to oxidative damage and

a variety of biological effects. These reactive intermediates are frequently produced photocatalytically following excitation of the semiconductor [4,5]. Reactive oxygen species and charge carriers, therefore, have been recognized as the main intermediates responsible for the photocatalysis as well as the antibacterial activity and cellular toxicity of semiconductors [5–10]. Because of the fundamental importance of reactive oxygen species in determining the photoactivity of semiconductors, the generation of reactive oxygen species can be considered, along with particle size, shape, band gap, and crystal structure, as an important intrinsic parameter determining the photochemical properties of semiconductors. If a framework can be built to identify and predict the generation of reactive oxygen species and reactivity of photoinduced electrons, it will be of great use in understanding the mechanism of semiconductor photoactivity and in evaluating or designing new materials. This current study aimed to develop such a theoretical and experimental framework.

Reactive oxygen species are not a single entity but represent a broad range of chemically distinct, reactive species with diverse oxidizing reactivity. Chemiluminescence and fluorescence are the

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most frequently used indirect methods for measuring reactive oxygen species. Chemiluminescent assays can measure $\cdot\text{OH}$, O_2^- and H_2O_2 levels but cannot distinguish these species [11]. Fluorescent probes can be easily used to detect O_2^- , $\cdot\text{OH}$, and $^1\text{O}_2$, but interference from other oxidants frequently requires additional HPLC analyses to definitively identify the reactive oxygen species [12]. Electron spin resonance spectroscopy (ESR) together with spin trapping is the most reliable and direct method for identification and quantification of short-lived free radicals and reactive oxygen species [13,14]. However, the lack of a standardized and systematic approach can lead to inaccurate identification of reactive oxygen species. For example, one study reported that photoexcited TiO_2 generated superoxide but another did not [15,16]. Moreover, it is difficult to identify photoinduced electrons using spin trapping. 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO), a ESR-spin label, has been used to elucidate electron transfer and the reactivity of electrons generated during photoexcitation of ZnO and ZnO/Au hybrid nanostructures [17,18]. The model system we have developed utilizes ESR combined with spin trapping and spin labeling techniques and can provide precise information about reactive oxygen species and electron behavior.

The theoretical approach used in the proposed model system relies on the link between band energy structures of semiconductors and chemical reduction potential of each kind of reactive oxygen species. Several investigators, using indirect methods, have reported that electronic band edge energies of a metal oxide strongly predict generation of reactive oxygen species [19–21]. The pioneering work of E. Burello and A. Worth demonstrated theoretically that the relative oxidative stress potential of metal oxide nanoparticles could be predicted from their band edge energies and the redox potentials of reactive oxygen species [19]. It has also been reported that the band edge energy of several types of metal oxide nanostructures is correlated with both generation of reactive oxygen species (measured with fluorescent indicators), and their photoinduced antibacterial activity [20]. While metal oxide semiconductors have received much attention, little research has focused on the generation of reactive oxygen species in metal sulfides [22,23]. Therefore, much is unknown about photogeneration of reactive oxygen species for metal sulfides. Metal sulfide micro–nano structures have received a great deal of interest due to their excellent solar spectrum responses, proper positions of the conduction and valence bands and high photocatalytic activities [24,25]. For example, more than 30 kinds of sulfide structures have been employed as photocatalysts [25]. We have therefore developed a framework in which photogeneration of reactive oxygen species and charge carriers can be experimentally determined by ESR and the formation of these species can be predicted theoretically using the band edge energy for study of metal sulfides.

For our studies, we synthesized four types of metal sulfide micro–nano structures (MNs) (e.g. CdS, ZnS, In_2S_3 , and Bi_2S_3). The chemical compositions of these materials were selected because they are metal sulfides widely used in photocatalytic applications. Spherical or quasi-spherical metal sulfides with combined micro- and nanostructures were prepared by a solvothermal method. Our primary objective was to establish a model system which combined theoretical and experimental analyses. Theoretical predictions were based on comparison of the band edge energy of a metal sulfide with the redox potential of individual reactive oxygen species. Experimental demonstration of the formation of reactive oxygen species was accomplished using ESR coupled with spin trapping and spin labeling techniques. This model was tested by examining the four selected metal sulfides semiconductors. Furthermore, we investigated correlations between the photocatalytic reduction and oxidation abilities and photogenerated electrons or reactive oxygen species in metal sulfides.

2. Materials and methods

2.1. Chemical and materials

Cadmium chloride, indium (III) chloride, zinc nitrate, bismuth chloride, sulfur, and absolute ethanol were analytically pure and purchased from Shanghai Chemical Reagent Co. Ltd. The spin trap, 5-tert-butoxycarbonyl 5-methyl-1-pyrroline N-oxide (BMPO), was purchased from Applied Bioanalytical Labs (Sarasota, FL). 4-oxo-2,2,6,6-Tetramethyl-1-piperidinyloxy (4-oxo-TEMP), 3,3',5,5'-tetramethylbenzidine (TMB), NaN_3 , and superoxide dismutase (SOD) were purchased from Sigma Chemical Co. (St. Louis, MO). 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) was purchased from Alexis, Enzo Life Sciences, Inc. (Farmingdale, NY). Milli-Q water (18 M Ω cm) was used for preparation of all solutions.

2.2. Synthesis of metal sulfide micro–nano structures (MNs)

In a typical synthesis, 0.5 mmol metal ions (CdCl_2 or $\text{Zn}(\text{NO}_3)_2$, or InCl_3) and 0.5 mmol sulfur powder (1 mmol thioacetamide for InCl_3) were added into a 28-ml Teflon-lined stainless steel autoclave. Then 21 ml absolute ethanol was added and the mixture was vigorously stirred. The autoclave was sealed, heated at 180 °C for 2–12 h, and air-cooled to room temperature. Finally, the precipitate was collected by centrifugation, washed several times with double distilled water and ethanol, and dried under vacuum at 50 °C. Bi_2S_3 micro–nano structures were prepared similarly by solvothermal methods [26].

2.3. Characterization

The crystal structure of as-synthesized products was characterized by X-ray diffraction (XRD, Bruker D8 Advance diffractometer) using monochromatized Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Scanning electron microscopy (SEM, Zeiss EVO LS-15) was used to characterize the morphology of metal sulfide micro–nano structures. Transmission electron microscopy and electron diffraction were performed with FEI Tecnai G² 20 at 200 kV accelerated voltage. The UV–vis absorption spectra were recorded on a Varian Cary 5000 UV–vis–NIR spectrophotometer. The BET surface areas of different metal sulfide micro–nano structures were determined by a Micromeritics Gemini 2380 specific area analyzer by measuring nitrogen adsorption.

For the comparison of reduction photocatalyzed by CdS, ZnS, In_2S_3 and Bi_2S_3 MNS, we examined the photoreduction of the TMB oxidation product. 5 ml 0.1 mg/ml TMB was firstly oxidized to TMB oxidation product (TMB*) by UV light (220 nm < λ < 320 nm). The TMB* solution was mixed well with 0.1 mg/ml photocatalyst and then irradiated with a WG320-filtered 450 W Xenon lamp to initiate the photoreduction reaction. The residual concentration of TMB* was determined after 5 min of irradiation by UV–vis spectroscopy.

The photocatalytic degradation of the methyl orange (MO) or rhodamine B (RhB) by ZnS, CdS, In_2S_3 , and Bi_2S_3 was evaluated in aqueous solutions. 20 mg of as-prepared photocatalyst was dispersed in a 50 ml aqueous solution containing 20 mg/l MO (or RhB). The solution was continuously stirred in the dark for 30 min to ensure that an adsorption–desorption equilibrium between the photocatalyst and dye molecules was established. Then, the suspension was irradiated using a 500 W Xenon lamp. During irradiation, the solution was stirred to maintain a suspension and the temperature was controlled by circulation of room temperature water around the sample. The pH values were about 6.0 and remained nearly unchanged before and after photocatalytic reaction for the four different metal sulfides. A 2 ml aliquot of the

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