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Photoelectrochemical reduction of nitrite ions to ammonia on CdS photocatalysts

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Abstract

The photoelectrochemical reduction of nitrite ions to ammonia on CdS photocatalysts was investigated in the slurry mode. The oxidation and the reduction reactions take place separately, thus, decreasing the electron–hole recombination and enhancing the yield of ammonia.

Keywords: Photoelectrochemical reduction; CdS photocatalysts; Ag/AgCl electrode

The reduction of nitrite ions is of importance for many reasons, such as remediation of pollutants and production of useful intermediate chemicals (for e.g. hydroxylamine). Although many studies have been reported on the electrochemical reduction of nitrite ions [1–3] studies on the photocatalytic reduction of nitrite ions to ammonia are limited [4–6]. The photoassisted reduction of nitrite anion to ammonia in alkaline aqueous sulfide solution was first achieved by illumination with visible light in the presence of CdS by Halmann and coworkers [4,6]. The drawback of the alkaline medium is that it would obviously be neutralized and acidified by nitrite ions. To the best of our knowledge, there are no reports on the photoelectrochemical reduction of nitrite ions to ammonia on semiconductor photocatalysts, although there is one report on the photoinduced electrochemical reduction of nitrite at a roughened silver surface [7]. In the present investigation, the photoelectrochemical reduction of nitrite on CdS is examined. The choice of CdS was based on the fact that it possesses a sufficiently negative flatband potential and good absorption in the visible region.

Powder semiconductors exhibit the disadvantage that the yield could be diminished by catalytic recombination. When aqueous dispersions of semiconductor powders are irradiated with photons of energy greater than the bandgap, electrons from the valence band can be excited to the conduction band, thus creating an electron–hole pair. The electron and hole can reduce and oxidize species in solution or recombine. For example, the hole can oxidize a water molecule to yield $^{\bullet}OH$ and the electron can reduce dissolved O_2 to give O_2^- or H_2O_2. When the rate of O_2 reduction is not sufficiently fast to match the rate of hole reaction, excess electrons will accumulate on the semiconductor surface and the electron–hole recombination will increase. Not available in small semiconductor particles is the considerable spatial separation of oxidized and reduced products found in photoelectrochemical cells. Electrochemical experiments have shown that electrons accumulated on the surface can be collected at an electrode to produce current [8–15]. In the present investigation, CdS powder suspended in an electrolyte is used to absorb the photon, while a collector (Pt disk) collects the resulting charges in an attempt to combine the advantages of a powder with those of a two-compartment electrolysis cell. The photoelectrochemical studies in the slurry mode were performed in a conventional three-electrode arrangement fitted with a quartz window as depicted in Fig. 1. The front of the illuminated compartment having the Pt disk electrode was illuminated using a 1000 W Hg lamp (Philips). The area of the quartz window is ~7 cm^2. The potential of the cell was controlled using a potentioscan (Wenking POS 73), coupled to a Keithley electrometer and a Philips (PM 8033) XY recorder. The working and counter electrodes were Pt disk (0.8 cm^2) and a Pt wire. The reference electrode was an Ag/AgCl electrode. The Pt electrodes were cleaned in concentrated nitric acid (3 M HNO_3) to remove any oxide layer. A Pt disk was used as the collector electrode because it has a large surface area to collect the CdS charge. The counter electrode was separated from the slurry compartment by a fine porosity glass frit. The CdS photocatalysts were prepared

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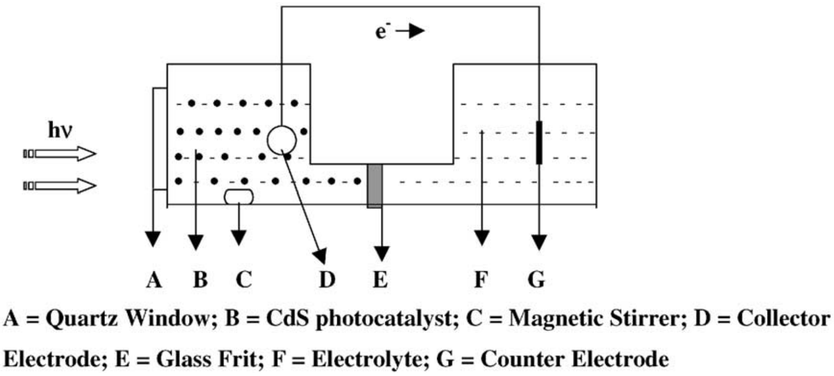

Fig. 1. Photoelectrochemical cell used for the reduction of nitrite ions to ammonia.

according to previous report [16]. In brief, CdS was precipitated by reacting $Cd(NO_3)_2$ and Na_2S (Analytical Grade, Merck India). The precipitate was filtered, washed several times with distilled water and calcined in air at 623 K and subjected to etching treatment with concentrated HNO_3 to remove $CdSO_4$, $Cd(OH)_2$ and/or CdO. X-ray diffraction patterns of calcined, etched CdS showed only the presence of hexagonal phase of CdS. The average particle size was determined to be ∼200 Å and the surface area was determined by the BET method to be ∼15 m^2/g. The metallized CdS catalysts were prepared by photodeposition method in the presence of methanol as reported previously [16]. In a typical preparation procedure, about 1 g of the semiconductor was added to 20 ml of double distilled water containing appropriate concentration of the noble metal chloride. Irradiation was carried out using a Xe lamp (Oriel Corporation, USA) for 4 h. Argon gas was bubbled through the solution during irradiation. After irradiation, the catalyst was filtered, washed several times with distilled water and dried in an air oven before use. The bulk metal content of the CdS catalysts were analyzed by Inductively Coupled Plasma Atomic Emission Spectrometer (ICPAES, Model 3410, ARL) after calibration with standard solution containing known metal content. The metal content was ∼1 wt.%. The CdS slurry in the illuminated compartment was stirred and purged with argon gas for 30 min prior to each measurement. The slurry consisted of 40 mg of CdS catalyst. A 50 ml each of 100 ppm nitrite and 500 ppm of sulfate was mixed thoroughly and 50 ml portion poured into the illuminated compartment and 50 ml into the second compartment. The cell was designed so that the particles in the slurry illuminated in the front of the compartment had to travel to cover a distance of ∼3 cm in order to discharge their excess charge at the Pt electrode in the back of the same compartment. The light absorbed by the back compartment was essentially negligible since the CdS slurry is optically dense and can be assumed to absorb all the light. The charge that is observed is hence only long-lived electrons or holes on the particles. The semiconductor suspension was vigorously stirred during the experiments. The solution was purged with argon for 30 min prior to each experiment.

The present authors have observed that the photocatalytic reduction of nitrite ions to ammonia is dependent on various experimental factors, such as pH, irradiation time, flat-band potential of the semiconductor, nature of the sacrificial agent and nature of the metal loaded on the semiconductor [16–18]. However, there are no reports on the photoelectrochemical reduction of nitrite ions on CdS particulates. Thus, it is of interest to explore the photoelectrochemical reduction of nitrite ions using semiconductor particles and assess their activity. The magnitude of current was independent of the position and the orientation of the collector electrode and decreased to essentially zero when stirring was stopped. This illustrates that the current originates from charges on bulk CdS suspension and not from light impinging on the collector electrode itself. A small current is also observed during irradiation, in the absence of CdS particles. The origin of this in unclear, but it has been ascribed previously to small photoeffects on metal electrodes [14]. Cyclic voltammograms showed a large increase in the cathodic current during illumination compared to the current in the dark. This indicates that the photocurrent is largely due to reactions of chemical species from the illuminated CdS. The ammonia formed (in the dark compartment) was estimated by the Indophenol method [19].

The yield of ammonia was dependent on the nature of the sacrificial agent. No ammonia was detected in an alkaline medium when sodium sulfide or a mixture of sodium sulfide and sodium sulfite were employed as sacrificial agents. When sulfite and sulfate were used ammonia was detected. However, the yield of ammonia was higher when sulfate was used and hence further studies were carried out using sulfate as the electrolyte. The results obtained from the photoelectrochemical studies in the slurry mode are shown in Table 1 and compared with the results obtained from photocatalytic studies. In the photocatalytic experiments, irradiation of CdS was carried out under similar conditions but in the absence of any electrochemical cell. The yield of ammonia is only marginally increased by metalization. No ammonia was observed when Pt/CdS was employed as the photocatalyst. When tests were carried out for ammonia, the solution turned white in contrast to the usual blue color. The

Table 1
Comparison of photoelectrochemical (slurry mode) and photocatalytic reduction of nitrite ions to ammonia on CdS photocatalysts

Photocatalyst	Yield of NH_3 (μmol)	
	Photocatalytic study	Photoelectrochemical study
CdS	0.06	1.53
Ru/CdS	0.38	2.53
Rh/CdS	0.13	2.23
Ir/CdS	0.12	1.92
Pt/CdS	–[a]	–[a]

Reaction conditions: 50 ml of 100 ppm nitrite, 50 ml of 500 ppm sulfate, 20 min irradiation, 40 mg catalyst, Pt working electrode at a potential of 0.1 V.

[a] No ammonia detected.

lack of detection of ammonia seems surprising since CdS irradiated in the presence of Pt electrode gives a photocurrent and nitrate can be reduced at the Pt electrode. However, when nitrite is placed only in the unirradiated compartment, an enhanced photocurrent (approximately twice) is observed and ammonia is detected in the dark compartment. X-ray photoelectron spectroscopic (XPS) study of Pt/CdS was investigated. A preliminary study of Pt/CdS catalyst showed that most of Pt (∼60–70 %) exists as Pt^{2+} in contrast to Ru^0/CdS, Ir^0/CdS and Rh^0/CdS. A detailed XPS study is in progress to characterize the surface properties of the metallized CdS catalysts and to correlate them with their photocatalytic activity. The yield of ammonia is approximately 6–25 times higher in the photoelectrochemical slurry mode compared to the photocatalytic mode. The counter Pt electrode is located in a compartment separated from that illuminated by a frit through which CdS particles could not pass. Thus, the reactions at the counter electrode does not interfere with the observations of the charge of the particles in the illuminated compartment. The collected charges are transmitted to the counter electrode in the other compartment through an external circuit so that the two types of charges can exhibit their oxidizing or reducing functions at separate places. Thus, enhanced yield of ammonia is observed in the photoelectrochemical slurry mode using CdS particles. A small yield of ammonia is normally observed in the illuminated compartment that corresponds to the direct electron transfer to nitrite. However, the yield of ammonia (∼0.2 μmol) is much lower compared to the one in the dark compartment. The electrochemical effects can be explained on the basis of the general model used in photocatalysis. Under bandgap illumination, an electron–hole pair is formed on the CdS particle surface as indicated by Eq. (1). Nitrite ions are reduced at the Pt electrode to give a large cathodic current via Eq. (2) leaving holes on the surface of CdS.

$$CdS \xrightarrow{h\nu} e^-_{c.b.} + h^+_{c.b.} \tag{1}$$

$$NO_2{}^- + 6H_2O + 6e^- \rightarrow NH_4{}^+ + 8OH^- \tag{2}$$

The holes react with CdS to give Cd^{2+} and S via Eq. (3)

$$CdS + 2h^+ \rightarrow Cd^{2+} + S\downarrow \tag{3}$$

which are not reducible the Pt electrode at the applied potential. This reaction (photocorrosion) is prevented to a large extent by the use of sacrificial agent, such as sulfide and sulfite ions. In the present study, sodium sulfate plays the role of a supporting electrolyte as well as sacrificial agent. This point needs further study and at the moment we are

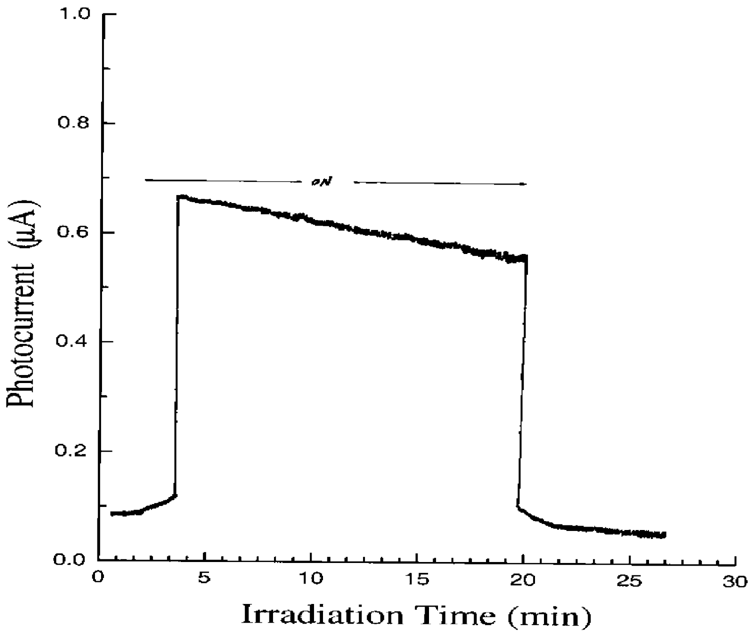

Fig. 2. Photocurrent vs. time for a stirred CdS suspension in a photoelectrochemical cell under argon atmosphere. Cell conditions: CdS powder (40 mg) in 50 ml of 100 ppm nitrite and 50 ml of 500 ppm sulfate solution, Pt electrode +0.1 V vs. Ag/AgCl.

unable to explain the exact role of sulfate ions. In the photoinduced reaction (3), the sulfide of CdS is the reducing agent. Hence, the photocatalyst degrades with time and consequently the photocurrent decreases with time. The slow (1–3 min) response of the current at the Pt electrode after illumination and the slow decay (3–5 min) in the dark are caused by the time required for the slurry particles to reach a stationary state in a time between excess charge generation during light absorption and charge gain/loss at the electrode. Fig. 2 shows the current collected at the Pt electrode from CdS slurry particles in argon saturated nitrite solution at + 0.1 V versus Ag/AgCl electrode. In order, to study the photocorrosion behavior, analysis of Cd^{2+} concentration in the illuminated compartment was carried out. It was observed that for the bare CdS, the concentration of Cd^{2+} after 5, 10 and 20 min of irradiation was 0.5, 1.8 and 2.9 μmol, respectively suggesting an increase in photocorrosion with increase in irradiation time. For the metallized CdS photocatalysts, the Cd^{2+} concentration was found to be about four times lower versus CdS alone. The potential scan during irradiation show two peaks which suggest the presence of two photoinduced electrochemical reactions that are not observed in the absence of irradiation. A detailed photoelectrochemical study is in progress to elucidate the mechanism of the photoelectrochemical reaction. The electrochemical measurements on semiconductor particles provide a direct method of characterizing the photocatalysts in situ and the present study demonstrates that such experiments may be extended to the study of other heterogeneous photocatalytic reactions by semiconductor particulates.

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